Water-based suspension of Polymer Nanoclay Composite Prepared via Miniemulsion Polymerization

A Thesis
Presented to
The Academic Faculty

by

Zhaohui Tong

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

School of Chemical and Biomolecular Engineering
Georgia Institute of Technology
December 2007

Water-based suspension of Polymer Nanoclay Composite Prepared via Miniemulsion Polymerization

Approved by:

Dr. Yulin Deng, Advisor
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Dr. Jeffery S. Hsieh
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Dr. J. Carson Meredith
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Dr. Timothy Patterson
School of Mechanical Engineering
Georgia Institute of Technology

Dr. Howard (Jeff) L. Empie
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Date Approved: October 11, 2007

To my husband Guanghui Lan and my son,Jesse

and

To my parents Duanxiang Tong and Hexiang Long,

ACKNOWLEDGEMENTS

There are many people who have helped me through my graduation education. First, I would like to thank my adviser, Dr. Yulin Deng, for providing me instruction, dedication, support, and encouragement through the entire PhD studying. I am also grateful for all of my committee members. Dr. Howard (Jeff) L. Empie, Dr. Jeffery S. Hsieh and Dr. J. Carson Meredith give me an invaluable source of advice and support for my research. I appreciate that Dr.Timothy Patterson takes his time to serve as one of my committee members for my defense and keep my science sound. I also thank Dr. Joseph Schork who is one of my committee members for my PhD proposal, and his advice and guidance are very important input of this research.

Next, I would like to thank all of my lab colleagues Dr. Zegui Yan, Dr. Qunhui Sun, Dr. Yunlin Zhao, Dr. Myungchul Park, Ying, Delong, Zhengzhi, Seyoung, Jihoon, Kim and Brett for the assistance for my lab work. I also thank Ms. Yolande Berta, Dr. Yong Ding and Mr. Shaobo Pan for their help for the TEM and SEM training and measurements. The fellowship from IPST member companies and the support from NSF(Grant Number CTS-0244371) is gratefully acknowledged.

Then, sincerely thanks go to Ms. Janet L. Webb for her grammar check of my dissertation. I also enjoy talking with her at all the time.

Finally, I would like to thank my family. I am deeply indebted to my lovely husband, guanghui Lan, for his always understanding, support, love and encouragement during my PhD studying and spend the hardest and happiest time in my life with me together, and my lovely son, jesse, for always bringing me the most happiness in my life. I would like to thank my parents, for their love, understanding and encouragement. This dissertation is especially for my lovely father, who has given me

his deepest love and provides me the freedom to do everything I like. In addition, Sincerely thanks go to my two brothers, who take their responsibility for taking care of my parents and support me at all the time. I also thank my parents-in-law to take care of my son for almost one year during my graduation study.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ABBREVIATIONS AND SYMBOLS

AIBN	2, 2-Azoisobutyronitrile
ABS	Acrylonitrile-Butadiene-Styrene Polymer
APS	Ammonium Persulfate
AMPS	2-Acrylamide-2-Methyl-1-Propane Sulfonic
BA	Butyl Acrylate
CEC	Cationic Exchange Capacity
CMC	Critical Micelle Concentration
CTAB	Cetyltrimethylammonium Bromide
DSC	Differential Scanning Calorimetry
DSD	Droplet Size Distribution
DVB	Divinylbenzene
EDS	Energy Dispersive Spectrometer
FTIR	Fourier Transform Infrared Spectroscopy

GMA	Glycidyl Methacrylate
GPC	Gel Permeation Chromatography
MFFT	Minimum Film Forming Temperature
MMT	Montmorillonite
MTAB	Meristyltrimethylammonium Bromide
NSC	Natural Saponite Clay
OTAB	Octadecyltrimethylammonium Bromide
PGMA	Polyglycidyl Methacrylate
PHEMA	Poly(2-Hydroxylethyl Methacrylate
PMMA	Poly(Methyl Methacrylate)
PS	Polystyrene
PSBA	Polystyrene Butyl Acrylate
PSD	Particle Size Distribution
P(St-GMA)	Poly (Styrene-Coglycidyl Methacrylate)
PVA	Polyvinyl Acetate
PVAC	Poly[Vinyl Acetate Chloride
SAN	Styrene Acryonitrile

SEM Scanning Electron Microscope

SSC Synthesized Saponite Clay

SLS Sodium Lauryl Sulfate surfactant

TEA Tensile Energy Adsorption

TFE Thermally-assisted Field Emission

TGA Thermogravimetric Analysis

THF Tetrahydrofuron

TEM Transmission Electron Microscope

TX-405 Triton 405

VBTAC Ar-vinylbenzyl Trimethylammonium Chloride

VOC Volatile Organic Compound

XRD X-ray Diffraction

SUMMARY

Polymer-clay composites, which contain at least one dimension in the range of 1-100 nm, have been very attractive in many applications because of their unique mechanical, thermal, electrical, and barrier properties. The nanocomposites, when applied as coating materials in paper barrier coating, are expected to improve the barrier properties without sacrificing mechanical and thermal properties, and thus solve one of the most challenging problems existing in current food and beverage packaging using paper barrier coating. A stable polymer composite suspension in an aqueous form has many other advantages such as better environmental concern, easier manipulation and better energy saving. However, the research of the preparation of polymer nanocomposite in a water suspension is quite limited in the literature. Furthermore, it is discovered in some current research that the encapsulation of inorganic materials inside polymer can result in better particle dispersion in the polymer matrix, strong physical or chemical bonding between polymer and nanoparticles. Hence, one interesting problem is whether we can improve the current water-based latex of polymer nanoclay composites with regard to its stability, dispersion and properties by encapsulating the nanoclay inside polymer.

Our previous research indicates that polymer nanoclay composites can increase barrier properties by about 300% compared to pure polymer system in paper barrier coating. That work focused solely on the coating formulation and properties. The fundamental mechanism has not been understood yet. If the mechanism and morphology formation of a stable aqueous polymer nanoclay composite are clarified, it will have great theoretical significance and provide guidance to the manufacturing

and optimization of the product. Therefore, this work focuses on the following three objectives:

- to study the impact of reaction conditions of the synthesis of a stable water-based nanoclay composite on final latex stability, encapsulation degree and the intercalation or exfoliation degree of nanoclay in the polymer latex
- to understand the fundamentals of the effect of nanoclay on the miniemulsion polymerization rate, conversion, molecular weight and kinetics
- to understand the impact of the inclusion of nanoclay on the physical or thermal properties of polystyrene (PS) and polystyrene butyl acrylate (PSBA) nanoclay composite films, which were made of the synthesized stable water-based suspension of polymer nanoclay composites.

In this study, miniemulsion polymerization has been determined as the synthesis approach to achieve the aforementioned objectives, since it enables the production of nanoscale particles dispersed into the aqueous phase and encapsulation of inorganic particles into the polymer droplets due to its predominating droplet nucleation mechanism. Moreover, two factors, the particle size of nanoclay and its surface functionalization, have been identified as the crucial ones to form a stable latex and encapsulate the nanoclay into polymer particles. More specifically, in our systems we utilized three types of nanoclays with different particle sizes, namely, montmorillonite (MMT-KSF), natural saponite clay (NSC), and synthesized saponite clay(SSC), and two surface modification methods, which differ in the selection of the modifiers, that is, either a cationic surfactant octadecyltrimethylammonium bromide (OTAB) or a monomer active surfactant ar-vinylbenzyl) trimethylammonium chloride (VBTAC). Their influence on latex stability and the formation of morphologies were investigated as well.

By using MMT-KSF as the nanoclay, we failed to synthesize a stable water-based suspension via a variety of emulsion and miniemulsion polymerization methods because of the large particle size of MMT-KSF (450 nm). By using NSC as nanoclay, a stable water-based polymer nanoclay colloids containing anisotropic saponite clay (NSC, 200 nm) platelets was produced by pre-modifying the nanoclay with cationic surfactant OTAB and via miniemulsion polymerization. The polymer-nanoclay composite obtained in this study has an intercalated structure and the final latex suspension is stable up to $5wt.\%$ clay in the polymer. However, the organophilic clay (NSC) was not encapsulated inside the polymer particles due to the large particle size of NSC. Finally, by using saponite SSC(50 nm) as the clay, a stable latex of polystyrene encapsulated nanoclay composite latex was successfully synthesized by pre-modified nanoclay with VBTAC.

After we successfully synthesized a stable latex of polymer nanoclay (SSC) composites, the impact of nanoclay on styrene miniemulsion polymerization mechanism was investigated. The results indicate that the nanoclay introduced in the system not only decreases the rate of polymerization, R_p, but also results in lowering reaction conversion, lowering M_w, increasing polydispersibility and the particle size of final latex in comparison to that of pure styrene miniemulsion polymerization. The reason for the hindrance of nanoclay on the styrene miniemulsion kinetics has been elucidated as well. Moreover, it is found that the inclusion of nanoclay can reinforce polystyrene(PS) and polystyrene-butylacrylate(PSBA) copolymer nanoclay composite films in almost all aspects of mechanical properties and improve thermal stability through the enhancement of T_m of PSBA and PS composite films. Finally, in a stable latex of polymer encapsulated nanoclay(SSC) composites, except the primary core-shell spherical particles, a small number of hemispherical particles also exists in the system. The mechanism to the formation of this variety of morphologies in the presence and the absence of nanoclay has been studied in this thesis.

CHAPTER I

INTRODUCTION

Water-based paper barrier coating has been widely used in many areas, especially in food packaging. More specifically, it has been applied in all the following food packaging areas such as quick service restaurant packaging, frozen foods, hot drink cups, milk and juice boxes, and meat and pet food packaging. It serves as a good coating material in combination of the benefits of coating suspensions and the paper substrate. Paper and paperboard have many advantages such as the porosity for penetration, good surface printability, the ease to be formed into the required shape, low toxicity, low cost and good biodegradability. However, the most important challenge in current water-based barrier paper coating is that the barrier properties (water or oil) of coating layers deriving from coating suspensions need to be further improved without sacrificing mechanical strength. A water-based suspension of polymer-clay nanocomposite is expected to provide the coating layer excellent physical and barrier properties because the exfolicated clay platelet with a high surface area is well dispersed in polymer matrix, and it can also increase tortuousity of the diffusion path. One researcher in our group prepared polymer/clay nanocomposite suspensions(PCNC), which exhibit superior barrier properties against water and water vapor of the coated linerboards [97]. That work indicates that the polymer clay nanocomposite suspensions have great potential to improve barrier properties as the coating dispersion applied for barrier paper coating. However, how to synthesize a stable water-based suspension of polymer clay nanocomposite has not been well known. Therefore, this dissertation primarily focuses on how to produce a stable water-based suspension of polymer clay nanocomposite and the fundamental understanding of its mechanism.

The current research of water-based dispersion has illustrated that the encapsulation of inorganic materials inside polymer can result in better particle dispersion in the polymer matrix, strong physical or chemical bonding between polymer and nanoparticles. Therefore, in this research, encapsulation technology was utilized to improve the current water-based latex of polymer nanoclay composites with regard to its stability, dispersion and properties. In general, in this dissertation, we focus on not only the preparation of a water-based suspension of polymer-nanocomposites bearing unique properties, but also the synthesis, the mechanism, and morphology formation of polymer encapsulated intercalated or exfoliated nanoclay platelets.

The main body of this work is organized as follows:

Chapter II offers the reader current development and applications of water-based paper barrier coating; the fundamental concepts, the mechanisms and principal applications of emulsion and miniemulsion polymerization; current development and synthesis methods of polymer nanocomposites; and current synthesis approaches of polymer nanocomposites with symmetric(core-shell) and asymmetric(hemispherical) morphologies.

Chapter III provides the specific objectives of this research. The feasible approaches to achieve these specific objectives are determined and some crucial issues are listed.

Chapter IV screens a list of emulsion and miniemulsion polymerization methods to synthesize a stable water-based suspension of polymer encapsulated nanoclay composite by using montmorillonite (MMT-KSF, the average particle size of 450nm) as the nanoclay. It focuses on how to produce a stable latex of polymer nanoclay composite through the effort in aspect of surface functionalization of nanoclay, polymerization approaches, polymerization process and conditions. Due to the large particle size of MMT-KSF, we failed to synthesize a stable polymer nanocomposite latex. Instead of MMT, the natural saponite clay (NSC) with the average particle size of 200nm was

selected as the clay candidate to use for the following research because of its small particle size and the formation of a stable suspension of organoclay in oil phase.

Chapter V presents an approach to synthesize stable water-based polymer nanoclay colloids containing anisotropic NSC platelets. The NSC clay platelet adhered on the surface of polymer particles but not encapsulated inside the particles because the small polymer particle(90-120nm) could not encapsulated larger clay particles. The work in this chapter also indicates that the surface modification of clay by a cationic surfactant octadecyltrimethylammonium bromide (OTAB) is critical not only for the formation of a exfoliated nanoclay but also for obtaining a stable miniemulsion.

Chapter VI further explores an miniemulsion approach to synthesize stable latex of polymer encapsulated the synthesized saponite clay (SSC) composite. The principle core-shell structural composite particles was successfully synthesized via miniemulsion polymerization by two important strategies: the surface modification of nanoclay by a monomer active surfactant ar-vinylbenzyl trimethylammonium chloride (VBTAC) and the inclusion of the nanoclay SSC with the average particle size of 50 nm. The nanoclay was exfoliated and a stable latex was formed as well. The final composite particles were principle spherical particles with the size less than 100 nm, and a small number of hemispherical or bowl-structured particles with the particle size ranging from approximately 100 to 1000 nm. The phase separation due to the existence of a large amount of hexadecane was accounted for the formation of a variety of morphologies. The mechanism to form this variety of morphologies in the presence of nanoclay and in the absence of nanoclay is presented in this chapter as well.

Chapter VII shifts to the investigation of the effect of organoclay on the kinetics of styrene miniemulsion polymerization. It was found that both the rate of polymerization R_p and the conversion degree decreased when increasing the amount of organoclay in the miniemulsion system. The hindrance of nanoclay on the polymerization rate and the fractional conversion is mainly caused by the destabilization of

the miniemulsion by the organoclay particles. The increase in the monomer viscosity and the decrease in the diffusion rate of the monomer and the living polymer inside the monomer droplet also accounts for the reduction in the polymerization rate.

Chapter VIII describes the physical and thermal properties of polystyrene (PS) and polystyrene-butylacrylate(PSBA) copolymer composite films in the presence of organoclay. It was found that the inclusion of nanoclay strengthens almost all of the mechanical properties of polymer or copolymer composites films. The thermal stability has also been improved with the enhancement of the clay content.

Chapter IX provides the overall conclusions and the possible future work of this research.

CHAPTER II

BACKGROUND

2.1 Water-based barrier coating

2.1.1 Development of coating technology

Coating is the process whereby a thin layer of material is deposited on a substrate. It is primarily used for surface protection and as such they provide a defense against chemical, mechanical and environmental threats by preventing water, oil or air penetration, chemical corrosion, UV penetration and electrical conduction. But they also function well for decoration purposes such as colorful decorating for buildings, printing materials, and various utensils.

About 30,000 years ago, cave dwellers drew cave paintings for decorative purposes. These cave paintings were based on the animal fat(binder)and the colored earth or other natural pigments (ochre) [110]. These amazing findings were the first discoveries to show the existence, the raw materials and technologies of the painting and coating in prehistoric time. Then, vegetable oils, animal fats and tree resins were used and continuously improved and modified to readily available domestic raw materials till contemporary time. Up to the twentieth century, vegetable products remained the most prominent raw materials for coating. At this time, because of the greater production and high quality coating demand of the society, an improved method of the paint manufacture was required and many new chemicals applied in coating were produced. Since the 1960's, the dramatic improvement had been made in the coating industry as aspect of the detailed characterization of properties and the functions of paint components [109]. In general, the current raw materials are mainly produced by the chemical industry as opposed to "cooked" from domestic materials.

Coating technology and application have continuously improved. The worldwide coating market in 2003 was estimated at about $70 billion. The markets in North America, Europe, and Asia are roughly equal in size, especially with the fastest grow of the Asia area. The value of coating shipments in the United States in 2002 according to the Current Industrial Report-Paints and Coating Manufacturing are shown in Table 1 [115]. Many industrial methods require materials that can not be manually applied. Many new technologies have been explored, such as waterborne coatings, radiation curable coatings, powder coatings and high-solids liquid coatings. The coatings without high level of volatile organic solvent content and the improvement of functional properties are still very attractive in current research.

Table 1: U.S. Coating Shipments,2002

Coatings	**Dollars**$\times 10^9$
Architectural	7.211
Product(OEM)	5.556
Special purpose	3.153
Miscellaneous	1.181
	17.101

Different recipes with different ratios and the combination of different organic or inorganic components allow coatings to be selective and have broad applications. Generally, the components in a coating recipe are classified into two groups. One group is volatile components including solvents, coalescing agents and condensation products. Another group is non-volatile components consisting of film-forming substances, resins, plasticizers, additives, dyes and pigments [41]. Film-forming substances, resins and plasticizers are generally called binders. Binders are materials that form the continuous film binding on the surface of a substrate. The binder governs the properties of the coating film predominantly. Resins are the most important part of the binder and include a variety of types, such as acrylics, alkyds, amino resins, cellulosics, epoxies, polyesters, urethanes, poly(vinyl acetates), poly(vinyl chlorides). Resins must be

soluble in either water or an organic solvent and they are applied to increase the performance such as gloss, softness or hardness, adhesion. Plasticizer is the oily organic component with a low molecular weight to decrease glass transition temperature of film-forming components. At the aid of plasticizer, a flexible and uniform film can be formed at a lower minimum film forming temperature (MFFT) [109]. In contrast, the excess of polymer resin or plasticizer can have deleterious effect on the film in an opposite way, either by making film too brittle or too soft.

Volatile components are in a large volume in all coating formulas. They evaporate during the film forming stage. Previously, almost all volatile components are organic solvents with a low molecular weight. Currently, many coatings have been developed that binder components are not fully soluble in volatile components. The high-solids coatings and waterborne coatings have been widely based on their advantages in terms of environmental concern, volatile organic compound (VOC) emissions and energy saving. High-solids coatings are to make coatings more highly concentrated and waterborne coatings are to use water as the major part instead of the volatile solvent [115].

Pigments are generally inorganic particles that are previously dispersed in the latex or the painting formula. They suspend in the binder after film formation. Generally, the primary purpose of pigment is to provide color, opacity to the coating film or reduce the cost of coatings. In recent research, by the selection of special functinonalized inorganic particles and polymerization methods, the unique morphology, such as core-shell, will be expected to disperse nanoscale solid materials (pigments, clays) better in order to eliminate the deleterious effect of pigments and meanwhile improve some functionalized properties such as physical properties, mechanical properties and barrier properties.

2.1.2 Waterborne Coating

The most significant development in the protective coating field since in the middle of nineteenth century was water-based paints. The new synthetic latex made the rapid growth of water-based coatings possible. About 1948, a styrene butadiene latex was produced and these paints immediately became popular because styrene-based latex had the following advantages: less odor, dry rapidly, easily clean-up tools, tough and washable wall finish. Then the invention of roll coating technology boosted the market of latex paints. The latex paints of the polyvinyl acetate (PVA) were introduced. About 1957, the first exterior water-based house paint based on acrylic type latices was introduced and the paint had the outstanding color retention on an exterior exposure [84, 113, 84].

The driving force of waterborne coating is increased legislative restrictions on the emission of organic materials to the atmosphere (VOC emission). It is the increased trend to replace the organic solvent by environmental friendly solution, water [103]. The first advantage of using water as a solvent is mainly because it is non-toxic and non-flammable which can reduce insurance premiums. The second advantage of using water as the solvent alleviates the odor problems and also decreases energy cost for curing because it reduces air flow through the ovens. Water has very unique properties when compared to most organic solvents. Table 2 shows the molecular weight, boiling points, evaporation rates and heats of vaporization of water and other typical organic solvents. However, due to unique properties of water, there are several problems by using water as the solvent. Water has a considerably higher boiling point ($212\,^{o}$F), heat capacity and heat of evaporation. Therefore, high energy is required for evaporation for waterborne coating than organic solvent coating. The surfactant is widely used in latex to reduce the surface tension of water and results in the improvement of pigment wetting. But in the presence of surfactant, water-based latex tends to give films poorer water resistance. Therefore the barrier properties

of waterborne coating need to be improved. In general, currently, the research in waterborne painting has focused on reducing or eliminating the toxic organic solvent usage, improving the water resistance, thermal and mechanical properties [70].

Table 2: Physical Constants of Solvents and diluent [70]

-	MW	B.P., ^oF	Evap. Rate	Heat of Vaporization, cal/gm
Low boiling point				
Ethyl ether	74	94	1	–
Ethyl acetate	88	171	2.7	102
Ethyl alcohol	46	173	7	204
Water	18	212	$30 - 40$	540
Toluene	92	231	4.5	87
Butanol	74	245	20	141
Cellosolve*	90	275	28	–
VM&P naphtha	–	$240 - 325$	7	–
Medium boiling point				
Xylene	106	286	9	82
Cyclohexanone	99	313	22	–
Cyclohexanol	100	322	150	108
Diacetone alcohol	116	336	60	–
High boiling point				
Tetralin	132	380	700	–
Benzyl alcohol	108	401	500	112
Isophorone	138	419	200	–
Carbitol acetate*	176	424	830	–

*Registered Trademark-Union Carbide Corp.

Latex-based coating as one type of water-based coatings, has been widely used in many areas for many years such as household applications, wall paints. The latex paints have numerous advantages such as rapid drying, low solvent odor, easy clean-up, reduced fire hazard, the durability and better long-term retention of mechanical properties. For example, the advantages of most popular latex paints, comprising acrylic, styrene-acrylic, and styrene-butadiene latexes, are their superior resistance to saponification, attainable shelf life and sometimes better adhesion. The polymer in latex coating exists as discrete particles, which do not move from one to another after

film formation. The films are formed by the coalescence at temperature higher than T_g. Moreover, the latex has high molecular weight, which provides super mechanical properties that are fully satisfied for many applications. Because its viscosity is independent on the molecular weight, the viscosity is still low at a high molecular weight. Therefore, it can be applied at relatively high solids [115]. The disadvantages of latex dispersion include the complicated synthesized process, the stability, heterogeneous components and low gloss. Dispersion systems are heterogeneous and they need a complicated make-up process by containing pigments, latexes, thickeners, defoamers, and other materials. The emulsion is easy to be broken by excessive handling due to its fair stability [83]. Therefore, the improvement of latex stability is very important to broaden its applications.

There are two categories for synthesis of polymer in water-borne coatings. One is that polymer synthesizes in the presence of water. Another is that polymer synthesizes in the bulk and in an organic solvent (usually water miscible) and subsequently adds to the aqueous phase. The synthesis methods as follows summarize the main procedures in the presence of water [83, 5].

- Emulsion polymerization
- Suspension polymerization
- Aqueous solution polymerization(i.e. both monomers and polymers water-soluble)
- Dispersion polymerization
- Polymerization in miniemulsions
- Polymerization in microemulsions

Emulsion polymerization is characterized by that a free radical initiator(usually

water soluble), a low water-soluble monomer, a water-in-oil system stabilized by surfactant and usually processing a radical polymerization. The ability of this polymerization procedure is utilized to prepare very high-molecular-weight polymers. Emulsion polymerization gives particles in the diameter range from nano-scale to micro-scale and enable to accurately control the particle size. Particle stability is achieved through the use of surfactant, sometimes in conjunction with the stabilizing effect of charged polymer end groups (e.g. sulphate groups for persulphate polymerization initiator) and ionic groups of ionic comonomers(e.g., carboxylate groups from acrylic acid and sulphonate groups from sulphoethyl methacrylate) [83].

Suspension polymerization takes place when a monomer soluble free radical polymerization initiator is used to polymerize essentially water-insoluble monomers. The polymerization kinetics in suspension polymerization is similar to those of bulk or solution polymerization. Particle is stabilized by using absorbed water-soluble acrylic acid copolymers and the particle size is generally in the range of 0.01-1 mm. As a result of the large particle size, suspension polymerization is seldom directly used in the form of the aqueous dispersion because of the problems from the settlement and film formation [5].

Free radical solution polymerization contains the monomer, the initiator, and the soluble polymer in the water or water/solvent mixture. The appropriate monomers used in this case include acrylic acid, acrylamide, N-vinyl pyrrolidone, and 2-acryamido-2-methyl-propane-sulphonic acid. This procedure is generally used for the preparation of dispersant and thickeners [5].

In dispersion polymerization, the monomer and the initiator are both soluble in the polymerization medium, which is a poor solvent for the resultant polymer. As for dispersion polymerization in the presence of water, a free radically initiated dispersion process has been described, in which the continuous phase is a miscible water/alcohol mixture and a copolymerizable surfactant is utilized [5].

Recently, the techniques of aqueous polymerization, such as miniemulsion, microemulsion have been greatly attractive in the practical exploitation in waterborne coating. Because this work uses miniemulsion polymerization as the primary approach to synthesize the water-based suspension of polymer nanoclay composites., Emulsion ,miniemulsion and microemulsion will be reviewed in detail in the next section in aspect of their mechanisms, properties and applications.

2.1.3 Water-based barrier paper coating

Typical applications of water-based coating are shown in Table 3.

Table 3: Typical application for water-based coatings [114]

Food packaging	**Non-food packaging**
Frozen/chilled food cartons	Ream & reel wrap
Pet food packaging	Poster and wallpaper
Candy boxes and wraps	Release paper
Fast food packaging	Building material wrap
Fish and vegetable boxes	Paper sacks
Cake/cookie packaging	Detergent cartons
Disposables	Corrugated board

The barrier flexible packaging using water-based coating shows great opportunities in food and beverage related areas. Many common food products-quick service restaurant packaging, frozen foods, hot drink cups, milk and juice boxes, and meat and pet food packaging-all use water-based barrier paper packaging. Paper and paperboard have many advantages as a substrate of water-based coating and present many advantages as good materials for food packaging. For example, they have the porosity necessary in some filling operations and good surface pritability. They also have the advantages of low toxicity, low cost, biodegradability and the ease to be formed into the required shape. Although paper and paperboard offer protection against light and dust, they lack of protection properties against moisture, gases, and odors. Therefore, in combination with other materials by coating or laminating with

polymeric materials, paper and paperboards are expected to satisfy the requirement for many product packagings [92]. For example, when water-based paper coating is utilized for food packaging, its barrier properties need to be further improved. There are a number of desirable properties required for barrier paper coating when it is utilized for food packaging [26].

- High resistance to water: paper substrates are notoriously sensitive to moisture. They lose their shape and strength characteristics by water-uptake. Ideally, a sufficient barrier layer is expected deriving from water-based coating formula.
- The coating paper should have high resistance to oils and greases from the materials stored inside the paper or from the external circumstance.
- The coating paper should be flexible enough to withstand folding and ceasing, be tough and scuff to retain its appearance during handling, and be anti-slip to prevent sliding of stacked packaging.
- The coating has to comply with food contact regulations.

More specifically, frozen and bakery products demand grease resistance and possible some other special properties such as the strength under low temperature. Some baked products or frozen products need to be heated or baked in the packages in a microwave or a standard oven. Hence, heat resistance is very important for the coated paper. Bakery packages also require appropriate water vapor resistance but maybe change its requirements based on different circumstances. For example, the storage bag should have good water vapor resistance to prevent the bread from drying. In contrast, when the bag is used to storage hot bread, it should allow the steam to escape from it. In general, the barrier properties under strict circumstances such as heating, cooling and freezing conditions require to be developed.

Development in new barrier coating materials and coating methods are very important to obtain the desirable barrier properties, mechanical or thermal properties,

and satisfy the requirement of current environmental regulations. First, the replacement of wax by recycling composites when they are coated on products such as corrugated containers is one important driving force. As for the coating methods, extrusion coating/lamination with various polyolefins are the major technologies currently. However, the polyolefins such as polyethylene are not recyclable or repulpable when they coat on the paper substrate. Due to the strict regulation on environmental concern, they have the limitation as the materials for barrier paper coatings. The extrusion coating, as a dominant coating method, requires a separate coater because of the speed and the width limitation or out-of-line configuration. However, different from the extrusion coating, water-based coating can be directly operated on line. The paper or paperboard of water-based barrier coating are recyclable and repulpable with a conventional pulping system. Generally, the driving force for these coatings are the desire for environmentally friendly packaging, taxation in central Europe or even direct cost savings. The objective of water-based barrier paper coating is to form a desirable barrier layer that prevents any substances from migrating into the containing materials from outside or from the paper coating layer itself. Water-based coating with desirable barrier coating formula is expected to provide paper and paperboard with a barrier against water, water vapor, grease and oil, gases and organic/inorganic impurities. In water-based polymer dispersion barrier coating, the latex is applied to the surface of paper or paperboard to form a solid, non-porous film after drying. The process is shown as follows. At the beginning, when water evaporates, the solid content increases and the distance between particles shrinks. Thereafter, particles lose their movability and flocculate together. As water evaporates, the void spaces are gradually filled by particle sliding and deformation. When water is almost completely evaporates, particles deform into a pore-free film. The coalescence of particles occurs by interdiffusion of polymer chains of adjacent particles [92]. According to DLVO (Derjaguin-landau-Verwey-Overbeek) theory, attraction energy has a primary

and secondary minimum value and between them there is maximum energy, namely energy barrier. Particles must go over this energy barrier before the coalescence occurs.

2.2 Emulsion and miniemulsion polymerization

2.2.1 Emulsion polymerization

An emulsion polymerization starts with water, surfactant, a water-insoluble (or scarcely soluble) monomer and a water-soluble initiator in an oil/water or water/oil system. The emulsion is formed by agitation at the aid of surfactant, which is called emulsification. The initiator is soluble in the medium, and not in the monomer in a classic emulsion polymerization. In this situation, the monomer is present predominately in the form of droplets (about 1-10 μm or larger). It is also present in the form of micelles if the surfactant concentration is higher than critical micelle concentration (CMC) and slight molecularly dissolved in the medium depending on the solubility of the monomer in the medium. Emulsion polymerization is the process, that is predominantly utilized for commercial polymerizations of vinyl acetate, vinyl chloride, acryamide, various acrylate copolymerizations, and copolymerizations of butadiene with styrene and acrylonitrile [80]. In general, emulsion polymerizations have been widely used in many industries such as synthetic rubbers, high-impact polymers, latex foams, latex paints, adhesives, binders, paper coatings, barrier coating additives because of their many advantages. First, heat generation can be easily controlled by heat transfer to the aqueous phase. Second, a greater rate of polymerization, the higher conversion and the higher molecular weight of polymer are obtained in emulsion polymerization than a equivalent bulk polymerization. A high conversion minimizes the residual monomer problem. Due to the high molecular weight, the molecular weight of polymer is easily controlled by chain-transfer agent. Third, because the continuous phase is water, the viscosity of emulsion polymerization is lower

than bulk polymerization and high solids latex can be easily transported. In addition, the water-based latex reduces both safety and environmental hazards [39]. For example, when coating the latex on the substrate, the low viscosity facilitates to spray on the substrate. Thereafter, when curing the coating on the surface, because of the rapid evaporation force of the aqueous phase, the polymer particles can coalesce together easily.

The motivation to carry out polymerization in water was because of the finding of natural rubber (polyisoprene in a latex). Natural rubber is the aqueous dispersion of polyisoprene particles and stabilized by surfactant-like protein. The beginning emulsion polymerization is the mimic of this natural rubber process. The major development of emulsion polymerization took place during the Second World War and it resulted in the process development of suspension and emulsion polymerization. In the period of the 1950s through to the 1980s, a variety of industrial products were developed but less mechanism principles guided their manufacturing. At the same time, the fundamental understanding of emulsion polymerization was carried out in many academic, government and industrial laboratories, for example: Fitch, Gardon, Vanderhoff, Ugelstad and Hansen [64]. In the United States, William D. Harkins developed a theory for the emulsion polymerization mechanism [44]. Then Smith and Ewart qualified Harkins' theory in 1948.

Harkins' theory [44] is based on the water-soluble initiator and the relatively insoluble monomer (for example styrene), which is immiscible with polymer. The Harkins' theory as shown in Figure 1 indicates that in the emulsion polymerization of a relatively insoluble monomer (styrene, isoprene, butadiene), almost every polymer latex particle is initiated in the monomer solubilized micelle. Firstly, the water-soluble initiator decomposes in the continuous phase to form a free radicals, which are then captured by present micelles. Micelles with a small amount of the solubilized monomer and free radicals are now initiated as the starting point of polymer particles. The large

monomer droplets in the continuous phase are the warehouse of the monomer and it diffuses across the continuous phase to enter the newly-initiated polymer particles. This newly-initiated polymer particles continue by the transportation of monomers from monomer droplets. As polymerization continues and polymer particles grow, excess free surfactant from the aqueous phase and other free micelles are absorbed to the surface of polymer particles and stabilizes polymer particles. When all the micelles are depleted, no new particle is initiated. The micelles disapear either by being nucleated by a free radical or by losing the surfactant required for the stabilization of existing growing particles.

The Harkins argued that micellar nucleation was dominant nucleation mechanism. Yet today it is argued that there are other possible sites where nucleation can occur. For example, homogeneous nucleation can take place when the surfactant concentration is lower than CMC and in surfactant-free polymerization. It is believed that particle nucleation, homogeneous nucleation and micelle nucleation coexist in the emulsion polymerization. However, for the most part, Harkins' theory still applies for the most case of the emulsion polymerization mechanism and other nucleation mechanism is often treated as secondary.

Smith and Ewart developed Harkins' theory and built a mathematical model for emulsion polymerization mechanism. Generally, based on Harkins' theory, the emulsion polymerization is divided into three intervals [39] as shown in Figure 2.

- Interval I: A rapid and transitory period with which emulsion polymerization initiates. It is characterized both by an increasing rate of polymerization due to particle nucleation and by the enhancement of the particle numbers. The monomer diffuses into polymer particles and polymer particles grow in size and contain the polymer as well as the monomer. The surfactant transferring from the micelle stabilizes polymer particles. The interval ends when all the micelles are depleted.

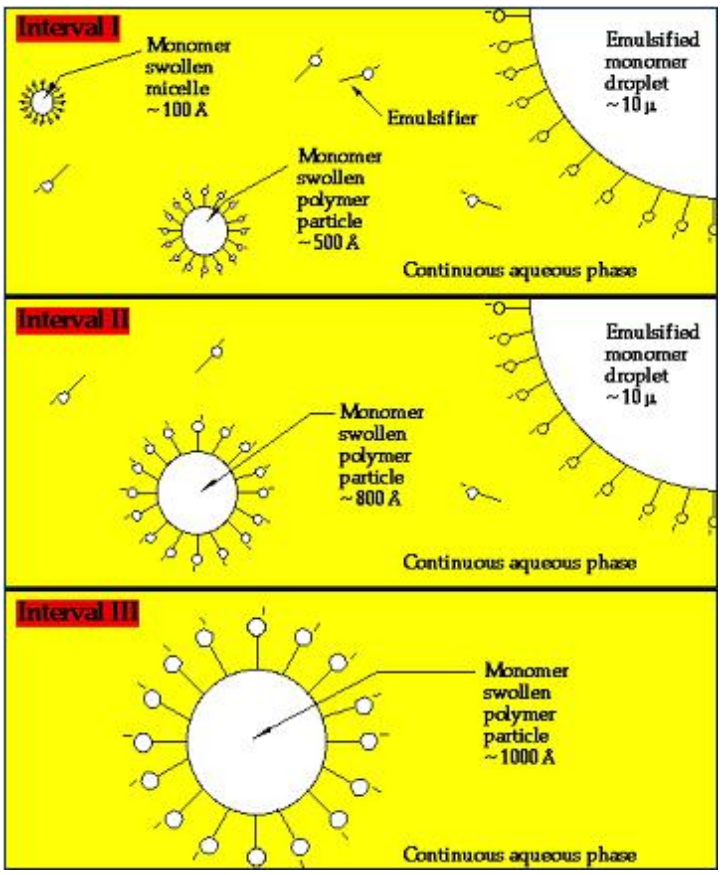


Figure 1: Harkins intervals of conventional emulsion polymerization [109]

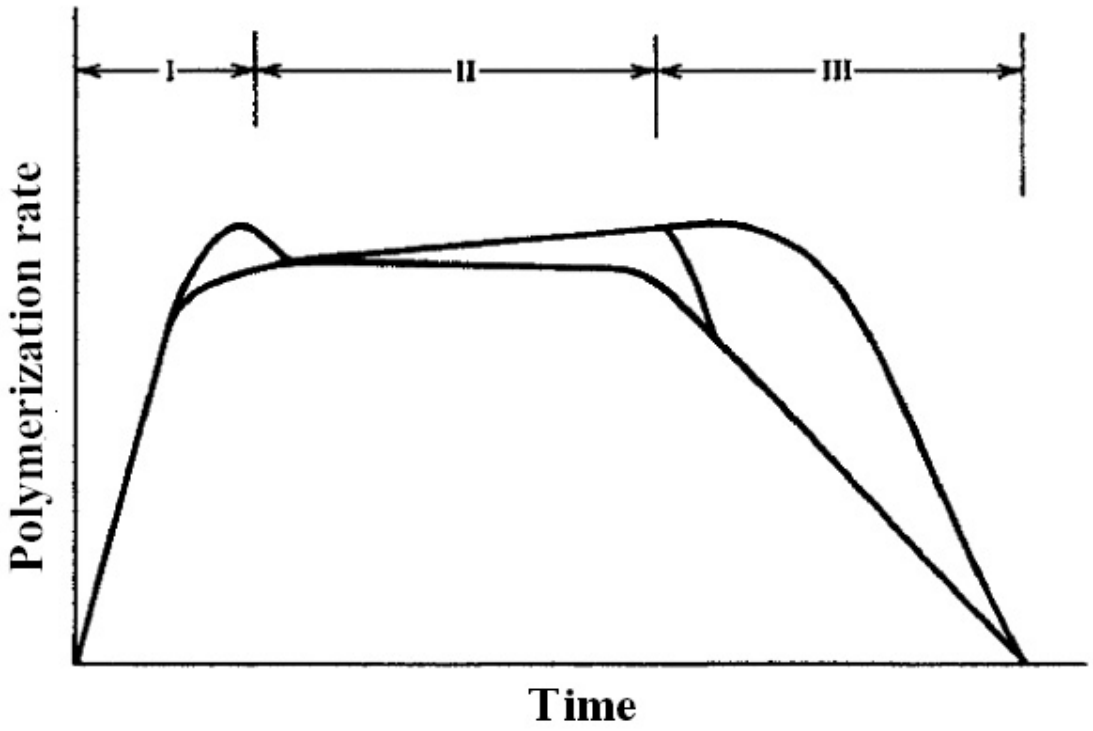


Figure 2: Different rate behaviors observed in typical emulsion polymerization [80].

- Interval II: Three phases are present: latex particles, the aqueous phase and monomer droplets. This interval is characterized by a constant rate of polymerization and a constant particle number. Latex particles have an approximately constant monomer concentration because of a balance arising between the free energy of mixing and surface energy effects. Polymer aims to be infinitely dilute into the monomer in terms of the free energy of mixing. But the contact between the swollen polymer particles and the continuous phase is limited, which is named as surfactant energy effect. The monomer transfers from the emulsion droplets through the aqueous phase, and into the latex particles to maintain a constant monomer concentration. Interval II ends when the monomer droplets disappear.

- Interval III: This is the final stage of the reaction. The particle number in this stage keeps constant as interval II. The rate of polymerization (the monomer

concentration) decreases when the remaining monomer consumes inside the particle. Monomer droplets eventually disappear. Only latex particles and the aqueous phase are present at the end.

The rate of polymerization R_p and the average number of radicals per micelle plus particle ($\bar{n}$) play a critical role to emulsion kinetics. The rate of polymerizationR_p in interval II and III depends on the propagation rate constant K_p, the monomer concentration$[M]$ in the particle and the concentration of active particles$[P\bullet]$ [80].

$$R_p = K_p[M][[P\bullet]] \tag{1}$$

the concentration of active particles$[P\bullet]$ is expressed by [80]

$$[P\bullet] = \frac{N^{'}\bar{n}}{N_A} \tag{2}$$

Where $N^{'}$ is the concentration of micelles plus particles, $\bar{n}$ is the average number of radicals per micelle plus particles, and N_A is the Avogadro number. When the two above equations are combined together and applied to Interval II and III, at that time $N^{'}$ substitutes by N (the particle number). The final equation is expressed by [80]

$$R_p = \frac{N\bar{n}K_p[M]}{N_A} \tag{3}$$

The value of $\bar{n}$ during interval II and III is critical to determine R_p. Generally, $\bar{n} = 0.5$ is applied for most emulsion polymerization when the system follows a zero-one kinetics. In this system, it is assumed that all particles contain either zero or one free radical. The presence of two radicals in one particle is similar with zero radicals since termination occurs so rapid and it is not a rate-determining step. As aspect of the overall polymer particles in the system, only half of them are active, therefore, in this case $\bar{n} = 0.5$. This combines case 1 and 2 Smith-Ewart theory. Case 1 of Smith-Ewart theory shows that in the case of small particle size and low initiator rates, $\bar{n} < 0.5$ if the desorption of radicals from particles and termination in

the aqueous phase are negligible. The case 2 of Smith-Ewart theory indicates that in the case of a large particle size and low termination in the aqueous phase, $\bar{n} > 0.5$. Two or more radicals are inside some fraction of polymer particles [39, 80].

2.2.2 Miniemulsion polymerization

In emulsion polymerization, large monomer droplets (1-10 μm) coexist with pure surfactant or monomer-swollen surfactant micelles before polymerization. During polymerization, the monomer diffuses from the larger monomer particles through the medium to micelles or new-initiated polymer particles. The micelle is the primary nucleation loci and the latex particle is not the primary emulsion droplet. In contrast, miniemulsion polymerization is the process that stable nanodroplets (50-500 nm) are dispersed in the continuous phase at the aid of high shear and an effective costabilizer to retard ostwald ripening. The monomer transferring through the water phase to micelles does not take place. The droplets themselves are the loci of nucleation and latex particle droplets are the ideal 1:1 copy of original droplets.

2.2.2.1 The development of miniemulsion

Miniemulsion is a heterophase system where stable nanodroplets about 50-500 nm are dispersed in a second continuous phase at the aid of an effective surfactant (costabilizer). The formation of miniemulsion relies on the combination of high shear treatment, surfactant, and costabilizer. The droplet surface area in miniemulsion is very large and all the surfactant is absorbed at the droplet surfaces and little free surfactant exists in the aqueous phase. In an ideal miniemulsion polymerization, the droplet becomes the primary locus of the initiation of the polymerization reaction and it is generally called "1:1 copy" of the droplet. Every droplet behaves as an independent reaction and polymerization inside droplets follows a suspension polymerization mechanism.

Ugelstad et al.[111] first proposed the concept of miniemulison. In this early

research, the styrene monomer was emulsified into a solution containing cetyl alcohol and sodium dodecyl sulfate. The water-soluble initiator potassium persulfate was used as the initiator in that research. The similiar size of droplets and particles were observed and it was proposed that nucleation primarily occurred in the droplet themselves in this "miniemulsions". Figure 3 shows the total number of papers per year published on miniemulsion polymerization. It shows, after a slow start, the number of publications in this field has risen rapidly.

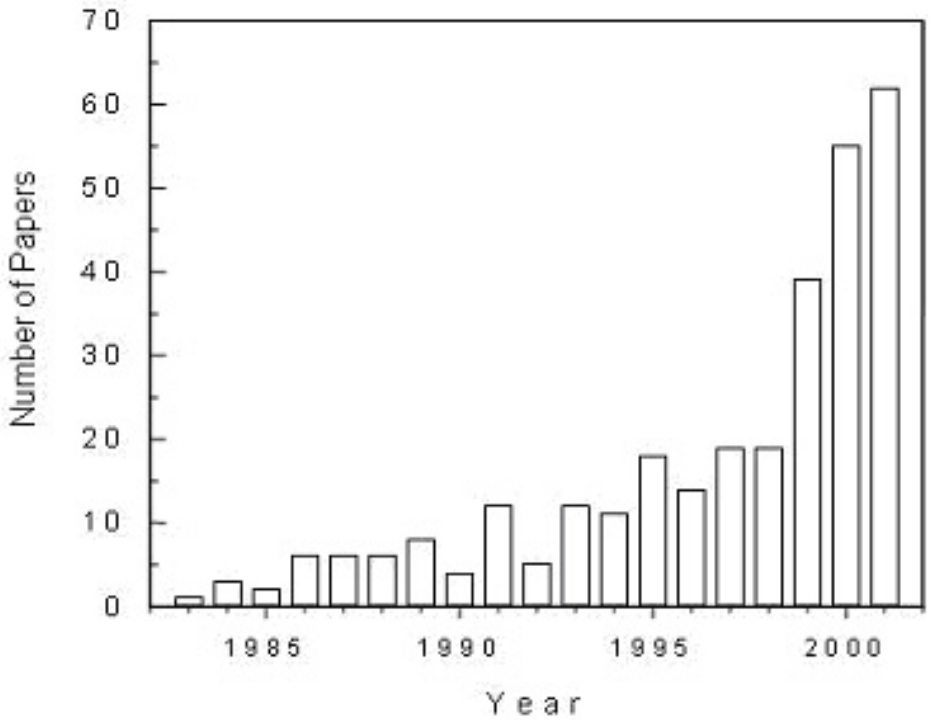


Figure 3: The total number of papers in miniemulsion polymerization [94].

In order to better understand the concept of miniemulsion, it is necessary to know the difference between miniemulsion polymerization and other heterophase emulsion polymerization types, namely microemulsion, macroemulsion (emulsion). A scheme of different processes is shown in Figure 4. A list of points of the difference of emulsion and miniemulsion are given as follows [56]:

- Emulsion is initially composed of large monomer droplets (1-10 μm) stabilized

by surfactant coexisted with empty or monomer-swollen surfactant micelles. Miniemulsion comprises stable nanodroplets (50-500 nm) at the aid of high shear and the costabilizer, which retards the monomer degradation.

- The micelle is the primary nucleation loci in emulsion polymerization. In miniemulsion polymerization, droplet nucleation is the primary nucleation mechanism and final latex particles are the copes of original droplets.

- During emulsion polymerization, the monomer diffuses from monomer droplets through the aqueous phase into micelles or newly-initiated polymer particles. During miniemulsion polymerization, the diffusion of the monomer does not occur.

- The size of latex particles is established by kinetic processes, where kinetic parameters such as temperature, the amount of surfactant, the amount of initiator play important roles. In miniemulsion polymerization, the size of latex particles is determined by the dispersion process and droplet stability. The kinetic parameters only play minor roles.

Both polymerization in microemulsions and in miniemulsions starts from a highly dispersed state. Their differences can be given as follows [120].

- Miniemulsion is osmotically stable at a stead state and critically stabilized with respect to colloid stability. However, microemulsion is a thermodynamic stable, spontaneously formed state.

- Interfacial energy between the oil and the water phase in a microemulsion is close to zero and complete surface coverage occurs in a microemulsion phase. In miniemulsion, miniemulsion requires high shear to reach a steady state of the stability and energy at oil/water interface is much larger than zero.

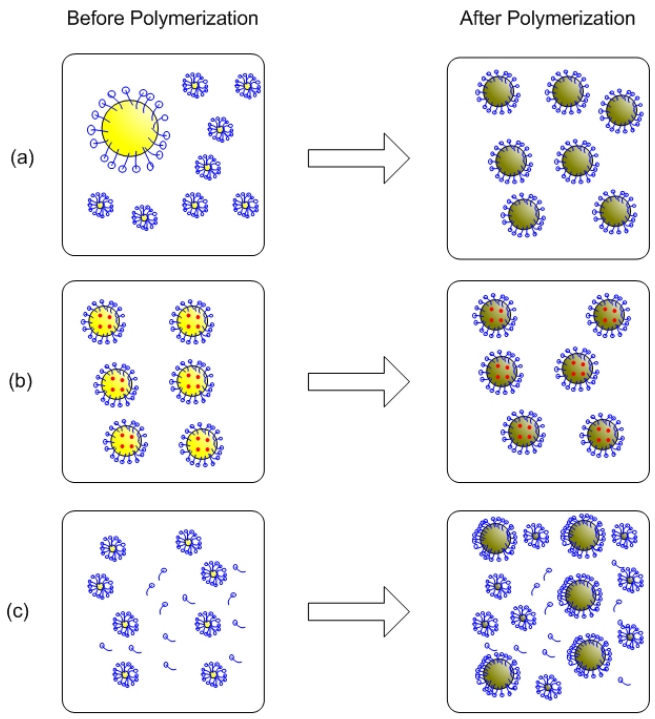


Figure 4: Comparison of different heterophase polymerization processes: (a) emulsion polymerization; (b) miniemulsion polymerization;(c) microemulsions [4].

- The formation of miniemulsion requires high mechanical agitation or shear forces to reach a steady state equilibrium of droplet fission and fusion, whereas the formation of microemulsion is usually spontaneous.

- The osmotic stability of miniemulsion droplets arises from a hydrophobe, which has extremely low water solubility and reduces the osmotic pressure. Final particles are the copy of the original droplets. In microemulsion polymerization, the osmotic pressure results in the destability of microemulsions and a majority of empty micelles exist.

- Final microemulsion latex comprises very small particles 5-50 nm in size, However final miniemulsion latex is composed of the particles in the range of 50-500 nm.

2.2.2.2 Miniemulsion mechanism and kinetics

The mechanism of miniemulsion nucleation is quite different than that of conventional emulsion polymerization. For an ideal miniemulsion system, droplet nucleation is expected to be the dominant mechanism. The formation of miniemulsion droplets arises from the high shear force to break up an emulsion into nanoscale particles. It also combines the function of an ionic or nonionic surfactant and a low molecular weight, highly water insoluble cosurfactant such as cetyl alcohol or hexadecane. The surfactant is required to retard the droplet coalescence caused by Brownian motion, settling and creaming following Stoke's law. The cosurfactant substantially retards the diffusion of the monomer out of droplets by limiting degradation by Ostwald ripening and it should be highly insoluble in the aqueous phase and highly soluble in the monomer droplets. As we know, the reduction in interfacial energy is the driving force for the formation of large particles from the degradation of small particles. The Ostwald ripening is applied for the degradation of small particles. After that, when the particles size become large enough for Stokes law, creaming takes place.

Theoretically, monomer droplet stability can be understood in terms of free energy. In a stable miniemulsion, the free energy for each droplet will equilibrate and the pressure difference is the same for each droplet. In a miniemulsion containing the monomer and polymer, the partial molar free energy by adding a second component to a droplet composes of the partial molar free energy of mixing and the interfacial partial molar free energy. From Huggins expression, the partial molar free energy of mixing can be combined with the interfacial partial molar free energy to give

$$\frac{\Delta \bar{G}_i}{RT} = \ln \phi_i + (1 - m_{ij})\phi_j + \chi_{ij}\phi_j^2 + \frac{2\bar{V}_i\gamma}{RTr} \tag{4}$$

Where ϕ is the volume fraction of monomer or polymer. m is the ratio of equilibrium number of molecular segments between the monomer and polymer. χ represents the interaction parameter between the monomer and polymer. γ is the surface tension at the interface of water and oil. $\bar{V}$ is the molar volume of the monomer, R is universal constant of gases and T is temperature. This equation clearly shows that the free energy increases as the phase diameter decreases. The smaller the monomer droplet, the less stable it is. Therefore, it becomes a driving force for the monomer to diffuse from a small droplet to a larger one. The costabilizer is applied to retard this driving force, namely, ostwald ripening. In miniemulsion with three phases, i.e., monomer droplets, the aqueous phase and polymer particles, the equal particle molar free energies are required for equilibrium conditions. In general, if ostwald ripening is prevented by the use of a costabilizer, the particle nucleation will be dominant [94].

The mechanism to stop ripening force in a miniemulsion is sketched by Figure 5. Suppose that the cosurfactant is perfectly water-insoluble and stays in the oil phase with the monomer. Suppose that the mixture of the monomer and the costabilizer behaves as an ideal mixture. Based on these hypotheses, the chemical potential or free energy for miniemulsion droplet system before polymerization can be expressed

as

$$\frac{\Delta\mu^{d}_{m,1-2}}{RT} = m_{m,h}(\phi_{m,1} - \phi_{m,2}) + \psi\left(\frac{1}{r_{d,1}} - \frac{1}{r_{d,2}}\right) \tag{5}$$

In macroemulsion, the two droplets have initially the same ratio of the monomer to polymer($\phi_{m,1} = \phi_{m,2}$). The difference in chemical potential is given by the difference in size only, where the monomer is transfered from the smaller droplets to bigger ones. When the costabilizer exists, this process increases the concentration in small particles and dilutes the concentration of costabilizer in big particles. A gradient in composition is created, which is presented by the first term on the right hand side of the above equation. Therefore, an opposite flow of the monomer is generated and eventually leads to an equilibrium between two terms of equation and a stable miniemulsion is achieved. In some literature, the equilibrium of the monomer in a miniemulsion are often expressed in terms of pressures. The droplet composition gives rise to osmotic pressure:

$$\prod_{osm} = RTc_m \tag{6}$$

whereas an interface generates a Laplace pressure inside the droplet, defined as follows:

$$\prod_{Lapl} = \frac{3\gamma}{r_d} \tag{7}$$

These equations [(5),(7)] can be unified to the one equation when the differences in osmotic and Laplace pressures between the two droplets is considered and when $m_{m,h}$ equal to 8/3 [94].

Although, most of research supports that the droplet nucleation predominates in miniemulsion polymerization, the homogeneous nucleation acting as a minor nucleation mechanism has also been reported as well. As we know, for a heterophase polymerization, two typical nucleation mechanisms, homogeneous nucleation (including micellar nucleation) and droplet nucleation are currently acceptable mechanisms by most researchers. Micellar nucleation only occurs at the concentration of free

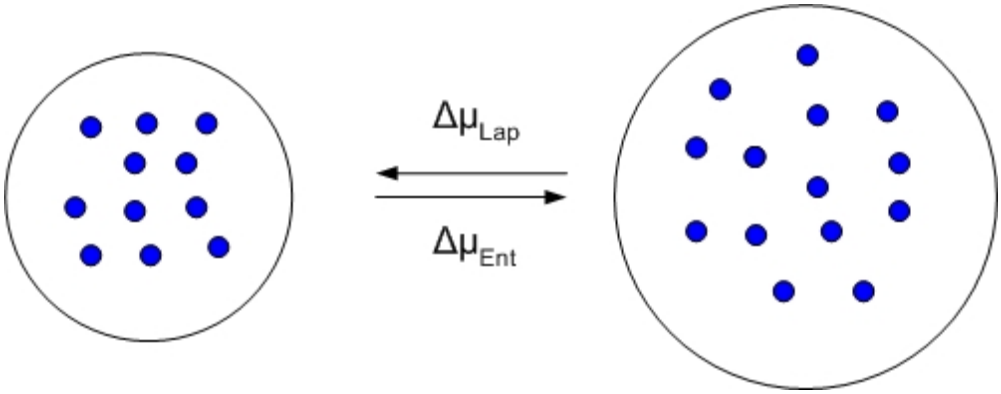


Figure 5: Schematic representation of the role of the hydrophobe in stopping the ripening process in a miniemulsion [94].

surfactant above the critical micelle concentration of the applied surfactant. The homogeneous nucleation occurs in surfactant-free emulsion polymerization, in that the latex seeds are formed from aggregating oligomers in the water phase and the monomer is diffused to the nucleation site (water phase). Homogeneous nucleation is the second possible nucleation mechanism in miniemulsion polymerization as reported by Choi et al. [25] (20% droplet nucleation in the case of cetyl alcohol as cosurfactant/hydrophober), Chern et al. [23] (55%-60% droplet nucleation in the case of dodecyl methacrylate and blue dye as hydrophobe respectively) and Reimers and Schork [90] (95% droplet nucleation in the case of hexadecane as hydrophobe).

As aforementioned, in emulsion polymerization, monomer transferring takes place from droplets to nucleated micelles in Smith-Ewart kinetics, which results in a constant polymerization rate as Interval II. However, interval II is absent in miniemulsion polymerization. One of the comprehensive kinetics studies of miniemulsion polymerization by Choi et al. [25] shows the quantitative kinetics analysis of styrene miniemulsion polymerization. Two following results were reported. Firstly, the particle-formation stage was unusually long, which contributed to the reduced rate of radical adsorption by monomer droplets. The fraction of active particles was determined by the loading level of the initiator. Secondly, miniemulsion polymerization

did not exhibit the interval II (a constant rate of polymerization stage) as conventional emulsion polymerization. This was because that the rate in interval II was determined by the monomer consuming rate inside the particles when almost all the particles initiated after interval I. Bechthold et al. [11] investigated the particle size development during polymerization and its dependence on the initiator concentration. They stated that droplet nucleation dominated if the particle size was independent of the initiator amount. In this case, the overall reaction rate did not depend on the amount of initiator but was only affected by the number of droplets or their size.

Figure 6 shows the calorimetric curve of a typical styrene miniemulsion polymerization with hexadecane as hydrophobe. Three distinguished intervals are detected through the process of miniemulsion polymerization. According to Harkins' definition for emulsion polymerization, only intervals I (particle nucleation) and III (particle growth) exist in minimemulsion polymerization. Moreover, as shown in this figure, interval IV (gel and glass effect) describes a pronounced gel-effect in miniemulsion. There is no interval II(propagation with a constant polymerization rate) shown in miniemulsion polymerization. This indicates that in dominant particle nucleation, the monomer diffusion is not the rate-determining step in miniemulsion polymerization.

2.2.2.3 The important properties of miniemulsion

- Oil soluble initiator: For miniemulsion polymerization, the initiator can be either oil or water-soluble. Water-soluble initiators dissociate in the aqueous phase, then adsorb to the particle surface, and then remain on the particle surface after initiation, unless chain transfer to the monomer occurs and the radical escapes into the aqueous phase [39]. Oil-soluble initiator is contained primarily within droplets and may initiate polymerization within droplets, except that the radicals experience a "cage effect" due to the finite size of particles. The cage effect produced by the newly formed radicals is unable to diffuse apart

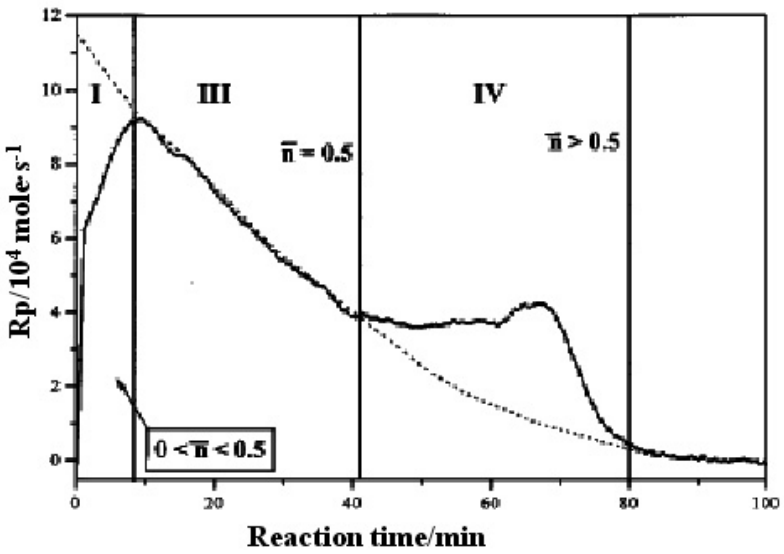


Figure 6: Calorimetric curve of a typical miniemulsion (styrene, SDS, KPS as initiator) [11].

before either recombining or terminating [18]. Two primary mechanisms have been proposed in the case of the oil-soluble initiator based on Smith-Edward "zero-one" assumption, which says that even number of radicals is similar to zero radical because of the recombination of radicals. Asua, et al. argued that radicals generated in the oil phase contributed more to polymerization, where one radical escaped after dissociation, leaving the other radical to propagate. Their results indicated that the initiator partitioned in the aqueous phase had a negligible effect on the particles [7]. Chern et al. stated that the oil-soluble initiator AIBN promoted nucleation in the monomer droplets [24]. The other mechanism, posed by Nomura and Suzuki, favored the initiator in the aqueous phase due to the strong cage effect for AIBN radicals to escape from a particle before termination. An initiator molecule dissociated in the aqueous phase, and a radical propagated until the oligomer was insoluble in water and therefore entered a particle. They demonstrated that only 10% of the initiator radicals were responsible for polymerization and these were formed in the

aqueous phase, based on a comparison to the water-soluble initiator potassium persulfate (KPS) [79].

- Choice of cosurfactant: It is well known that destabilization of nanodroplets by ostwald ripening can efficiently be slowed down by the addition of a hydrophobic agent to the dispersed phase which counteracts the laplace pressure of the droplet. It is important to choose an agent, which can hardly diffuse from one droplet to the other and therefore is trapped in each droplet. Standard choices for hydrophobes or costabilizers are: hexadecane and cetyl alcohol. Ugelstad et al. [111] firstly stated that long-chain alcohols could be used as cosurfactant for their ability to aid the effectiveness of anionic emulsifier in stabilizing their oil-in-water emulsion. Then El-Aasser et al. found that the minimum hydrocarbon chain length for stability enhancement was twelve carbon units. Tang et al. [100] reported that broad particle size distribution of miniemulsion was obtained even when a high efficiency microfluidizer was used to create the miniemulsion. The choice of potential hydrophobes is widespread: beside hexadecane as a model, hydrophobic dyes, polymers, comonomers, plastisizers or other additives can be used. Silanes, siloxanes, isocyanates, polyester, fluorinated alkanes and many others also turn out to be very efficient in suppressing ostwald ripening [4]. However, although in literatures many costabilizers are acted as osmotic agents to block monomer ripening, hexadecane as hydrophobe has been used as a model for the miniemulsion polymerization. Earlier researchers found that hexadecane was more effective than alcohol due to its ability to produce low polydispersity of particle size distribution. Frontenot and Schork (1993) [38] revealed that systems containing hexadecane as the costabilizer were less sensitive to the charge of surfactant and interaction between surfactant and cosurfactant. More recently, Reimers and Schork [90] reported that miniemulsion could achieve 95% droplet nucleation using hexadecane as costabilizer, namely

as robust nucleation.

- Miniemulsion stability: To create a stable miniemulsion, the droplets must be stabilized against molecular diffusion degradation (ostwald ripening or $\tau 1$ mechanism) and against coalescence by collisions ($\tau 2$ mechanism). Before emulsification, the homogenization devices break up particles into miniemulsion. As reported by Delgado et al. [27] and Gooch et al. [42], the miniemulsion stability towards centrifugation enhanced with the surfactant concentration, the costabilizer concentration and the sonication time. After emulsification, monomer miniemulsions degraded because of monomer diffusion, costabilizer diffusion, settling or creaming, and droplet coalescence. Colloid stability is usually controlled by the type and the amount of the employed surfactant. Recent work on steady-state miniemulsions exhibited that cationic surfactants from well-defined miniemulsions latex had a narrow size distribution and high stability [56]. Their research depended on the latex particle sizes on the amount of different surfactants. It showed that ionic surfactants could be more efficiently employed for the synthesis of small particles than the nonionics, whereas nonionic surfactants were better suited for synthesis and stabilization of large particles. With respect to the encapsulation of pigments, the chemical parameters of miniemulsion, such as the amount and the type of the surfactant, had to be restrictly selected so that the final size of latex corresponded with the size of the pigments [12]. It was stated that the destabilization of nanodroplets by ostwald ripening could efficiently be slowed down by an addition of a hydrophobic agent to the dispersed phase which counteracted the pressure of the droplet. In general, it is important to choose an agent, which can hardly diffuse from one droplet to the other and therefore is trapped in each droplet. The effectiveness of the hydrophobe increases with decreasing water solubility in the continuous phase.

Using an adequate amount of hydrophobe and undergoing an efficient homogenization process, a steady-state miniemulsification is reached. After stopping sonication, an equilibration process has to occur where the effective chemical potential in each droplet (which can be expressed as an effective net pressure) is equilibrating. The particle size of rapidly polymerized minidroplets does not or does just weakly depend on the amount of the hydrophobe [4].

- Particle size distribution: Because miniemulsion is originally formed by a shear or ultrasonification process, the droplet size distribution before polymerization is supposed to be broader, therefore, the resultant particle size distribution (PSD) (after polymerization) will have a large polydispersity. Landfester et al. demonstrated that the PSD of miniemulsion could be either broader or narrower than its macroemulsion. In most cases, minimeulsion will have a polydispersity equal to, or only slightly greater than the equivalent macroemulsion [94].

  Droplet size distribution (DSD) affects directly both miniemulsion stability and droplet nucleation and it becomes the most important characteristic of miniemulsion. Therefore, the understanding of mechanisms ruling miniemulsion polymerization strongly depends on an accurate determination of the DSD(or PSD). Table 4 summarizes the techniques used to measure the average droplet size and the DSD.

Table 4: Methods used to measure the average droplet size and its distribution [8]

Authors	Method
Azad et al.	$O_sO_4$staining/hardening of styrene droplets/TEM
Uglestad et al.	Free surfactant in the aqueous phase
Choi et al.	Freeze-fracturing following by replication/TEM
Van Hasmersveld	Cryo-TEM
Erdem et al.	Soap titration
Miller et al.	CHDF
Several authors	Light scattering
Landfester et al.	SANS

Among these methods, light scattering has been frequently used to determine the droplet size of the monomer or latex. This technique is very rapid and easy to operate. However, vast dilution is required to avoid multiple scattering. The dilution has an influence on the PSD by the desorption of surfactant and by dissolution of the monomer/polymer in the aqueous phase. In order to minimize this effect, the dilution in this research is made by using the solution, which has the same concentration of surfactant as the mother liquor. In this dissertation, Malvern Zetasizer 3000 was used because of precise temperature control and easy for manipulation. When this measurement is applied to miniemulsion polymerization with a broad PSD, repeatability is approximately 30 nm under strict controls of its diluted concentration. Essentially, the mechanism of this light scattering measurement is called photon correlation spectroscopy (PCS), which measures the velocity of particles diffusing due to Brownian motion. The instrument measures the diffusion coefficient (D) and converts this to size (S) using the Stokes-Einstein equation [45].

$$D = \frac{KT}{3\pi\eta S} \tag{8}$$

PSD provides the entire characterization of the dispersion systems. The common way of dispersion system characterization is based on the average parameters, which arises from the fist or second order of PSD. The "mean diameter" on the number basis is defined as follows:

$$\langle d \rangle^{number} = (\sum_{1}^{21} w_i(\log(d_i))\Delta\log(d_i)/d_i^2)/(\sum_{1}^{21} w_i(\log(d_i))\Delta\log(d_i)/d_i^3) \tag{9}$$

The PSD polydispersity is characterized by "standard deviation" which is defined as a square root of a sum of PSD square deviation on a linear scale around

a weight size. It is calculated as

$$\sigma = \sqrt{\sum_{1}^{21} w_i(\log(d))\Delta\log(d_i)(d_i - \langle d\rangle^{weight})^2} \tag{10}$$

2.2.2.4 The application of miniemulsion polymerization

Many advantages of miniemulsion have boosted the development of many new applications in recent years. Major advantages of miniemulison polymerization are listed as follows:

- Morphology controlling: In miniemulsion polymerization, the droplet nucleation is dominanting and monomer transfer through the aqueous phase is absent, which makes it possible to control the particle morphologies and compositions. Reproducibility of particle morphology is expected by the ideal 1:1 copy of the droplet before and after polymerization.

- Particle size distribution: The particle size distribution is easy to be controlled based on the following two mechanisms. Firstly, the monomer droplet size distribution in miniemulsion polymerization does not solely depend on the droplet size distribution induced by a homogenizer or a sonicator, but thermodynamical swelling equilibrium. Secondly, the chance for monomer transportation by mass transfer is eliminated in miniemulsion polymerization.

- Production of high-solids and low-viscosity latex: Because of the polydispersity of miniemulsion, a broad size distribution can be obtained by adjusting polymerization parameters. The polydispersed latex show a lower viscosity, as a result, the solid content in a latex can be increased and lower shipping costs and less water can be achieved.

- Shear stability: Miniemulsion latexes have shown more stable than conventional macroemulsion latexes under the same shear conditions. The reason arises from

the greater ratio of N_0/N_f in macroemulsion than that in miniemulsion, which means that a small number of large particles may act as the seeds of aggregation.

- Production of highly hydrophobic polymer: Because of mass transfer limitation in macroemulsion polymerization, the highly hydrophobic monomer can not transfer from the monomer droplet to the micelle and make it impossible to produce high conversion of the polymer. In miniemulsion polyemeration, the droplet nucleation eliminates this transfer and make it possible to produce hydrophobic polymer.

- Nanoencapsulation: Miniemulsion is a direct and reproducible method to obtain nanoencapsulation due to its particle size of 50-500 nm, its dominating particle nucleation mechanism and no monomer mass transfer during the polymerization. Generally, if an organic or inorganic solid is pre-dispersed in the monomer phase and after emulsification, it stays inside the monomer droplets and therefore nanoencapsulation may be obtained by miniemulsion polymerization.

2.3 Polymer nanoclay composite

The term "nanocomposite" describes a two-phase material where one of the phases is dispersed in the second one on a nanometer ($10^{-9}m$) scale. This term is commonly used in two distinct areas of material science: ceramics and polymers. However, in this dissertation, we will only consider nanocomposites based on polymers. Nanocomposites are commonly based on polymer matrices reinforced by nanofillers such as precipitated silicas and silica titanic oxides synthesized by the sol-gel process, silica beads, cellulose whiskers, zeolites as well as colloid dispersion of rigid polymers and many others [54]. Intercalation of inorganic layered materials into polymers is also an excellent way of constructing novel inorganic-polymer nanoassemblies [102]. Among these polymer nanocomposites, intercalated compounds of inorganic layered

materials with polymers have many unique properties such as excellent mechanical properties, low water sensitivity, permeability to gases and heat seal.

Polymer-clay composites or hybrids are divided into three general types as shown in Figure 7. In conventional composites, the clay acts as the conventional filler and forms an aggregated layered structure. In a intercalated nano-composite, a regular insertion of polymer in between clay galleries occurs and 1 nm -thick clay layers are dispersed in the polymer matrix to form a monolithic structure. The clay galleries lose their entire registry and are well dispersed in a continuous polymer matrix. In an fully-exfoliated polymer-clay nanocomposites, the average gallery height is solely determined by the clay silicate contents. The exfoliated (delaminated) polymer-clay nanocomposites display better stiffness, strength, and barrier properties with far less inorganic content than that used in conventional particulate-filled polymer composites. Generally, the larger the degree of exfoliation in polymer-clay nanocomposites, the greater is the enhancement of these properties [20].

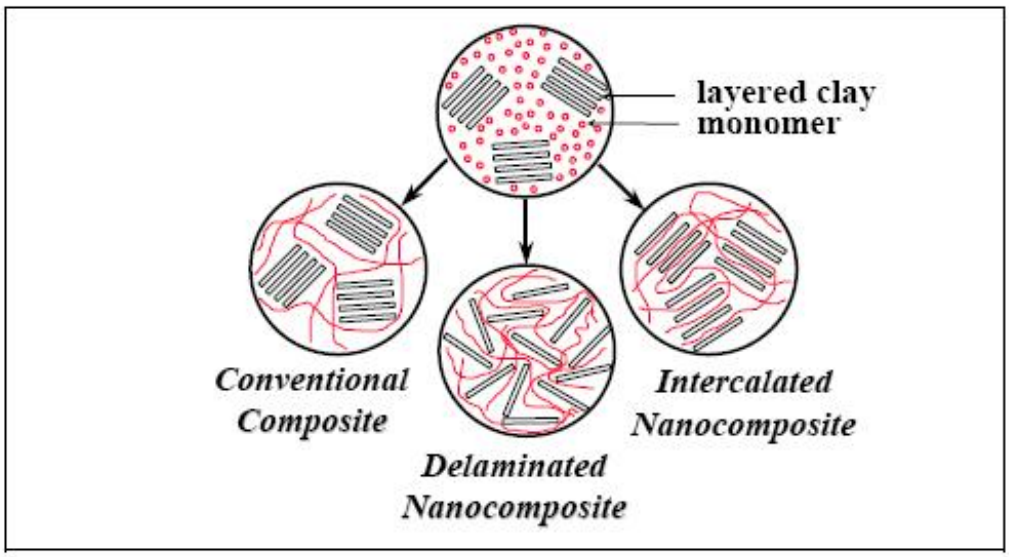


Figure 7: Three structures of polymer nanoclay composite [54]

2.3.1 Surface modification of nanoclay

Clay minerals are composed of a certain group of layered crystalline silicate minerals (phyllosicates and related minerals). Minerals include Micas, Vermiculite and Smectites. An important feature of both smectites and vermiculites is their ability to exchange cations between the interlayer and a coexisting aqueous solution. In this dissertation, we will focus on the smectite family of clay minerals such as MMT, saponite. A layer of minerals of the smectite group is composed of one central octahedral sheet sandwiched between two parallel tetrahedral sheets, condensed into one unit layer designated as 2:1 or "tetrahedral-octahedral-tetrahedral" (TOT). The montmorillonite structure following a TOT layer structure is shown in Figure 8 [91]. In MMT tetrahedral layers consisting of [SiO_4]-tetrahedrons enclose the [M(O_5, OH)]-octahedron layer (M, mainly Al, Mg, but Fe is also often found). Isomorphous substitutions of Si^{4+} and Al^{3+} in the tetrahedral lattice and of Al^{3+} for Mg^{2+} in the octahedral sheet cause an excess of negative charges within the montmorillonite layers. These negative charges are balanced by cations such as Ca^{2+} and Na^{2+} stayed between the layers. Due to high hydrophilicity of the layer, water molecules are usually also present between the layers. The stacking of the layers leads to gaps called interlayers or galleries, which arises from van der waals force. MMT and saponite have very similar structure except the difference of the compositions of the substituted cations and the particle sizes. The ideal chemical composite of MMT is

$$[(Al_{3.50-2.80}Mg_{0.50-1.20})(Si_8)O_{20}(OH_4)]Na_{0.50-1.20} \tag{11}$$

The ideal chemical composite of saponite is

$$[(Mg_{6.00})(Si_{7.50-6.80}Al_{0.50-1.20})O_{20}(OH_4)]Na_{0.50-1.20} \tag{12}$$

The interlayer d-spacing with the single layer thickness of 9.6 ^oA represents the repeat unit of the multilayer material. The d-spacing is calculated from the (001)

harmonics obtained from X-ray diffraction patterns. On a large scale, each layer can be seen as a high aspect ratio lamella about several hundred nanometer in diameter and $1nm$ in thickness (for montmorillonite). Five to ten layers are associated by interlayer ions in primary particles (8-10 nm in the thickness direction) and in turn form the large irregular aggregated structure with 0.1-10 mm in diameter [9].

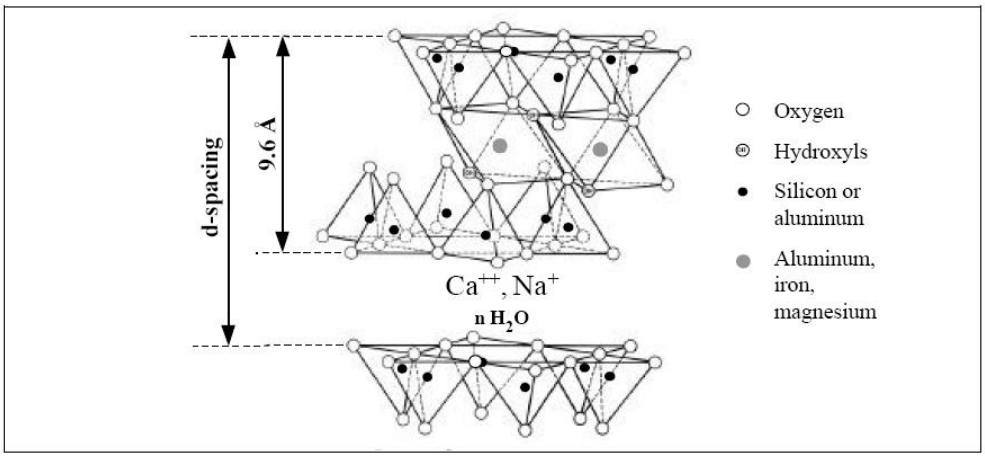


Figure 8: Idealised structure for montmorillonite, proposed by Hoffmann, Endell and Wilm, showing two tetrahedral sheets fused to one octahedral sheet. The gray and black dots indicate the locations of isomorphous substitutions in the octahedral and tetrahedral sites, respectively [54].

Because clay is hydrophilic, it is not compatible with most polymers and must be chemically modified to render its surface more hydrophobic. The most popular surface treatments are organic ammonium cations, which can be exchanged for inorganic cations existing on the silicate surface. The primary exchange of the metallic cation by the organic ammonium cation is usually carried out in aqueous systems. The driving force for this reaction is the tendency of the hydrophobic organic tails to be drawn away from the aqueous system and the tendency of the small inorganic cations to be fully hydrated in the aqueous system. The longer the aliphatic chains that comprise the cation, the stronger will be the tendency of the cation to be drawn

away from the aqueous system. It is now common to synthesize effective organophilic clays by replacing the metallic cations by quaternary ammonium cations of the type $[(CH_3)_3NR']^+$or$[(CH_3)_2NR'R'']^+$, where R' and R" are aliphatic and aliphatic or aromatic substituents, respectively [118]. The replacement of inorganic exchange cations by organic onium ions on the gallery surfaces of smectite clays not only serves to match the clay surface polarity with the polarity of the polymer, but it also expands the clay galleries. This facilitates the penetration of the gallery space (intercalation) by polymer precursors or the performed polymer.

The active end group can physically adsorb or covalently attach to the inorganic particle surface to further improve the interfacial interaction of the clay with the monomer. This active end group can be the initiator or the active vinyl monomer. Because the processing complexity and the manipulating difficulties of grafting initiator on the clay surface, in this dissertation, the research limits on the active monomer not the initiator. One major approach of surface functionalization on silica particles or clay is using alkoxysilane compounds. The organic functional groups are introduced onto the surface of silicate particles through the condensation reaction between silanol group (Si-OH) of the silica surface and the alkoxysilane compounds. However, some drawbacks accompanies this reaction route. First, some silanol groups of the alkoxysilane compounds might remain in the product owing to the incompletion of the dehydration reaction. These silanol groups are highly reactive and might cause further condensation reactions during the period of the storage and the usage of formed nanocomposites [49, 36]. Moreover, the high cost of the alkoxysilane compounds also limit their practicability in mass production. Several other surface grafting on the inorganic particles has been reported. Graft polymerization of glycidyl methacrylate (GMA) on to the surface of alkyl nano-SiC was carried out, resulting in composite particles with SiC core and polymeric shell in which polyglycidyl methacrylate (PGMA) was chemically attached to the nanoparticles by the double bonds introduced during

the pretreatment with a coupling agent [68]. Chemical functionalization on nano-scaled silica particles was performed through the reaction between the silanol group of silica and the oxirane ring of epoxy compounds in the presence of tin chloride as a catalyst [62]. Finally, the surfactant with the active group double bond, such as oleic acid, VBTAC and head- or tail-type surface active monomers, HC-8, HC-10, HC-18, HC-ole, TC-10, TMC-10 and TA-10 could adsorb or covalently graft on the inorganic materials surface, and consecutively spontaneous polymerization took place [28, 120].

2.3.2 Synthesis methods of polymer nanoclay hybrid

The methods to synthesize polymer nanoclay hybrid include in-situ polymerization, common solvent method, polymer melt intercalation methods. In-situ polymerization was the first method to synthesize polymer nanocomposite based on polyamide 6 [81]. Firstly, the organoclay is swollen in the monomer and then the polymerization is initiated by the addition of the curing agent or increasing temperature. The driving force of this "in-situ polymerization" is the interaction between monomer moleculars and the organoclay, which depends on the surface treatment of the clay, the polarity of monomer molecules and the condition of swelling. Figure 9 illustrates that polar monomer molecules diffuse between the clay layers at the aid of alkylammonium ions and the final polymerization reactions result in the delamination of the clay. Polar solvents can be used to synthesize polymer-clay nanocomposites by firstly dispersed the organoclay in a solvent such as toluene or Tetrahydrofuron (THF), and then polymer, which can be dissolved in this organic solvent, is added to the solution and intercalated into the gallery of clay layers. Finally the solvent is removed by evaporation under vacuum. The driving force of this method is that the entropy gained by desorption of solvent molecules compensates the decrease in the conformational entropy of the intercalated polymer chain. This method is beneficial to make the non-polarity polymer nanocomposite. However, the usage of large quantities of solvent

hinders the industrial application of this method [87]. The first melt intercalation was reported by Vaia et al. in 1993 [112]. It involves the mixing of the layered silicate with the polymer in the molten state above its softening point. Melt intercalation of polystyrene and its derivations have also been studied using this technique. The polymer chain lose their conformational entropy as they intercalate between the clay layers, which is compensated by enthalpic interactions between the clay and the polymer. The melt intercalation process has large potential for the industrial applications [54].

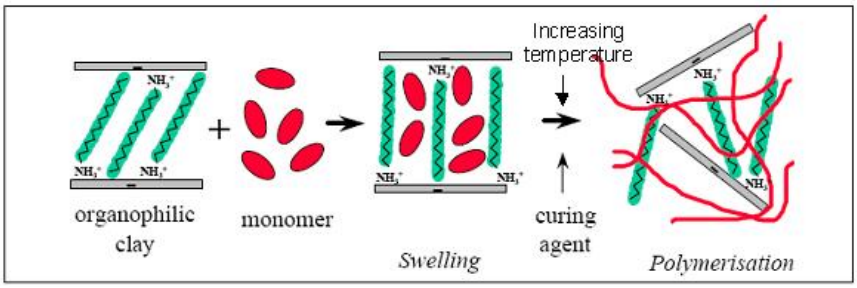


Figure 9: The diagram of in-situ polymerization [87]

The most recent works in nanocomposite materials have focused on bulk and solvent polymerization and less on the preparation of functional water-based nanocomposite suspension. In this research, our objective is about to synthesize water based suspension. Here we will focus on the methods which can form water-based suspension. Recent researches reported that one-step emulsion polymerization could offer a new approach to the synthesis of a nanocomposite. One-step emulsion method is a new and simple process of direct intercalation without using organically modified silicate or coupling agents but instead using a usual one-step emulsion technique. An emulsion system consisting of an aqueous medium can contribute to the affinity between the hydrophilic host and hydrophobic guest by the action of the emulsifier. Furthermore, the emulsion polymerization has the advantage of being able to simultaneously attain both high molecular masses and high reaction rates. Myung

H. N., Dong C. H. [77] prepared non-extractable styrene-acryonitrile copolymer-montmollironite (SAN-MMT) nanocomposites by two different intercalation process: (1) a usual one-step emulsion copolymerization in the presence of the Na^+-MMT; and (2) a solution copolymerization with MMT modified by dimethyl dehydrogenated tallow ammonium. Many physicochemical properties, such as polymer loading into the interlayer of MMT, molecular masses of the intercalated polymer, gallery expansion, thermal stability, mechanical properties, and the dispersibility of MMT in the polymer matrix of the emulsion product are found experimentally to far exceed those of products derived from the solution polymerization [78]. The Epoxy-clay hybrid, Acrylonitrile-butadiene-styrene polymer (ABS) and a Na^+-exchanged MMT were described by direct intercalation through one-step emulsion polymerization [50]. Polyaniline -Na^+- montmorillonite suspension and SAN-clay Nanocomposite suspension have been synthesized by emulsion polymerization successfully [53, 52]. Xu et al. [117] described a method to synthesize exfoliated poly (styrene-co-methyl)/clay nanocomposites through an emulsion polymerization by using reactive surfactant, 2-acrylamide-2-methyl-1-propane sulfonic (AMPS), which was claimed to make the polymer end tethered on pristine Na-MMT. Huang and Brittain [48] synthesized the poly(methyl methacrylate) (PMMA)-layered silicate nanocomposites by suspension polymerization and emulsion polymerization. They simply mixed the unmodified clay into the aqueous phase or added the clay in post-polymerization step. The final products obtained were not thermodynamically stable water-dispersion latex but in form of aggregates. Herrera et al [46] synthesized the water-based polymer/clay nanocomposites by first chemically modifying the laponite clay minerals by silant agents (-methyacryloxy propyl mono-, di, tri-methyl ethoxysilane) before polymerization and then proceeding with seeded emulsion polymerization. However, the stability of final latex was not reported. All of these indicated that the use of emulsion polymerization is proved to be of great importance in preparing substantial polymer-clay

hybrid nanocomposites. In addition, this emulsion technique can also contribute to eliminating toxicological and environmental problems.

2.3.3 Properties of polymer nanoclay composite

In aspect of the nanocomposites with enhanced properties, the clay nanoclayers must be uniformly dispersed (exfoliated) in the polymer matrix, as opposed to being aggregated as tactoids or simply intercalated. Once nanolayer exfoliation has been achieved, the improvement in properties can be manifested as an increase in tensile properties, as well as enhanced barrier properties, decreased solvent uptake, increased thermal stability and flam retardance [54]. Firstly, the tensile and toughening improvement can be attributed to the tremendous surface area of the clay in the polymer matrix, which facilitates stress transfer to the reinforcement phase. Conventional polymer clay composites containing aggregated nanoclayer tactoids improve rigidity, but they often sacrifice strength, elongation and toughness. However, exfoliated clay nanocomposites, such as those that have been achieved for nylon 6 and epoxy systems, have shown improvement in all aspects of their mechanical performance. In general, high aspect ratio nanolayers provide mechanical properties' improvement that is not possible for larger-scaled composites. Secondly, Blumstein [87] first reported the improved thermal stability of a polymer clay nancomposite that combined polymethylmethacrylate (PMMA) and montmorillonite clay. Although the high clay loading (mass fraction -10% intercalated PMMA) would undoubtedly affect the properties dominated by the inorganic phase, the indications of the enhancement of polymer thermal properties are clear. Blumstein argued that the thermal stability of PMMA-nanocomposites was due not only to its different structure, but also to the restricted thermal motion of the PMMA in the gallery. More recent studies of improved thermal stability were reported in both a polydimethylsiloxane-clay nanocomposite and in a polyimide-clay nanocomposite. Fianlly, the impermeable clay layers mandate a

tortuous pathway for permeation to transverse the nanocomposite as shown in Figure 10. The nanocomposite has excellent barrier properties against oxygen, nitrogen, carbon dioxide, water vapor, gasoline, etc. The improvement of barrier properties comes from the hindered diffusion pathways through nanocomposites.

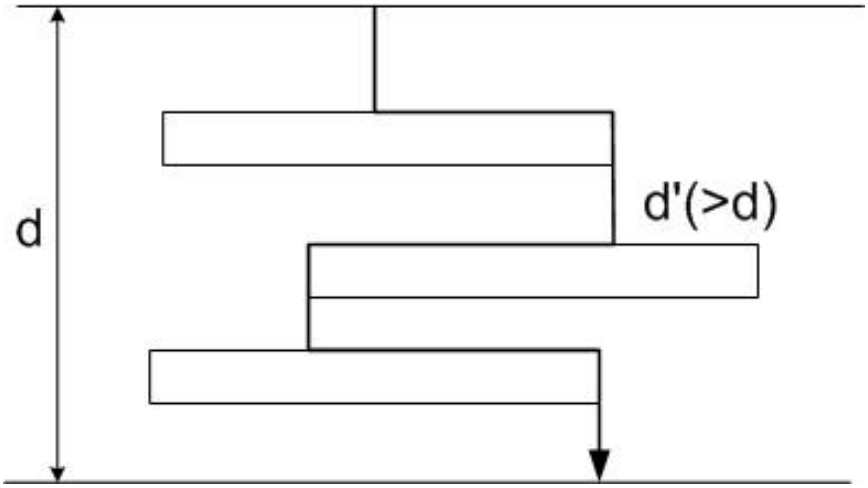


Figure 10: Model describing the path of the diffusing gas through the nanocomposite [59]

2.3.4 The characterization of polymer nanolcay composite

There are mainly two methods to characterize the structure of polymer-clay nanoclay composites. The most straightforward one is X-ray diffraction because it is a good way to evaluate d-spacing of nanoclay galleries. Transmision electron microscopy (TEM) is a powerful technique to study submicron particles and their structures. It is widely applied for the study of nanoparticles. In our system, nanoparticles in the water phase are perfectly suitable for TEM measurement. Moreover, SEM (scanning electron microscopy) is another powerful technique to investigate submicron particles. The results combining TEM and SEM generally provide complete information for the morphologies of nanoparticles.

2.3.4.1 X-ray diffraction

Figure 11 shows the sketch of the diffraction from two scattering planes (i.e. two consecutive clay layers) that are separated by a distance d (i.e. d-spacing) at the incident angle θ. The experimental 2θ value is the angle between diffracted and incoming X-ray waves. The wave normals connect points of identical phase for incident and diffracted waves. Since the direction of d is normal to the planes, and the wave is normal to the wavelength, so the angles opposite A and B are also θ. Thus, $\sin\theta = A/d = B/d$ so that $(A + B) = 2d\sin\theta$. Moreover, the distance (A+B) equals to $n \bullet l$ (a whole number of wavelength) for total constructive reinforcement to occur between the scattering from these phases.Thus, a constructive interference occurs when:

$$n \bullet \lambda = 2 \bullet d \bullet \sin\theta \tag{13}$$

This equation is known as the Bragg law. The integer n refers to the degree of the diffraction. It means, for instance, that if $d_{001} = 10^0 A$, then $d_{002} = 5^0 A$, $d_{003} = 3.33^0 A$ etc [54].

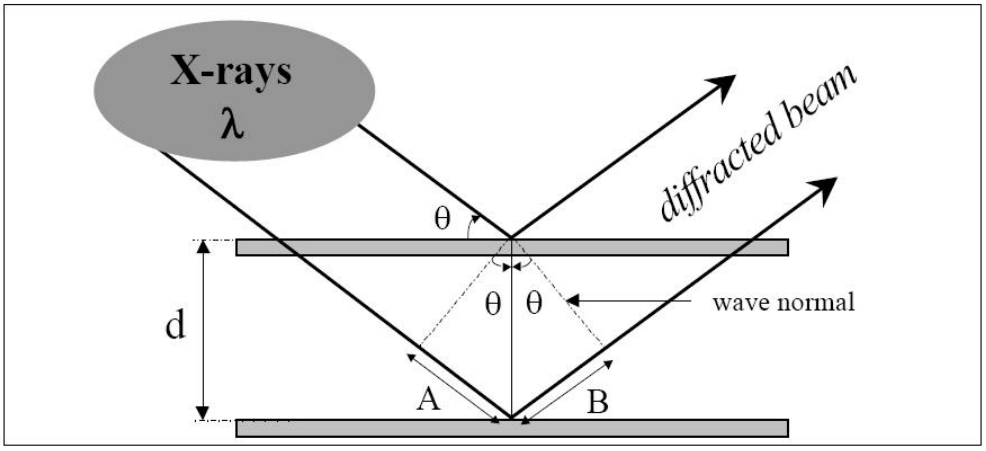


Figure 11: The X-ray powder diffractometer [54].

2.3.4.2 Transmission Electron Microscopy

In transmission electron microscopy (TEM), image formation is due to the scattering of electrons as the electron beam passes through the sample. A transmission electron microscope can be divided up into three components: the illumination system comprises the gun, which produces the electrons and the condenser lenses equipped with a diaphragm, which provides the beam onto the specimen. The electrons are scattered as they pass through the specimen. Then, they are transferred to the objective lens. The first image of specimen is formed by the objective lens, where the spread of electron beam is controlled by the objective aperture and gives contrast to the image. The imaging system uses several lenses (intermediate lens and projector lens) to magnify the image and focus it on the viewing screen where the operator can observe the magnified image of the specimen.

2.3.4.3 Scanning Electron Microscopy

The scanning electron microscope (SEM) is a type of electron microscope capable of producing high-resolution images of a sample surface. Generally SEM images have a three-dimensional appearance and are very useful for the surface morphology of the sample. The spatial resolution of SEM is determined by the electron spot size which in turn depends on the magnetic electron-optical system which produces the scanning beam.

In comparison with TEM, SEM has the advantages including the ability to image a comparatively large area of the specimen; available for measuring the composition of the specimen in combination with EDS; and much easier to interpret than TEM images. The high-resolution (between less than 1 nm and 20 nm) SEM is available in the laboratory of Georgia Tech and is utilized in this thesis.

2.4 Synthesis of polymer nanocomposites with symmetric and asymmetric morphologies

Nanotechnology is to create new materials, devices, and systems in a submicron scale by physical and chemical approaches. Generating nanostrutural materials by self assembling technique in nanometer scale is the essence of nanotechnology. Nanotechnology is expected to have a broad range of applications in many industries. The U.S. National Science Foundation has predicted that the global market for nanotechnologies will reach $1 trillion or more within 20 years. Two strategies are generally employed for generating nanostructures. One is "top-down", that is, small features are made by starting with larger materials and patterning to make nanoscale materials with a precise pattern. Another is "bottom-up", that is, to build organic and inorganic structures atom-by-atom, or molecule-by-molecule by a variety of methods such as molecular synthesis, colloid chemistry, polymer synthesis methods [19]. In the bottom-up approach toward nanomaterials, the nanobuilding block itself must be synthesized and then these nanobuilding blocks assemble together into the expected structures with desired properties. In attempt to prepare complex nanomaterials with a designed structure such as symmetrical (e.g. core-shell) or other asymmetric (e.g. hemispherical) morphologies, the chemical structure must be strictly controlled and the nanobuilding block is functionalized in a molecular level. With respect to the synthesis of a water-based suspension of polymer nanocomposites, the control of the particle morphology is an essential part of producing high quality latex products for applications in coatings, adhesives, impact modifiers, and medical diagnostics areas. Thereafter, we will review the current development for the preparation of the micro or nano-scale core-shell(asymmetric) and the asymmetric nanobuilding block, the two morphologies existing in our synthesized polymer nanoclay composites.

2.4.1 Synthesis of polymer encapsulated nanoparticle composite

Recently, encapsulation techniques have commanded considerable interest because of its functions as protection, delivery or release controlling and better dispersion. First of all, the function of encapsulation is protection by isolating the core from its surrounding harsh environment. For example, encapsulation protects probiotic bacteria from high temperature food processing and assists passage through the digestive system; encapsulation protects products from oxidation and moisture in food and pharmaceutical industry; encapsulation protects enzyme from denaturing by solvent. Encapsulation can also be used to deliver potential toxic materials, such as pesticides and herbicides in agricultural and environmental applications. Secondly, the function of encapsulation is to control or delay the release. In pharmaceutical application, encapsulation will allow for targeted release of the encapsulated ingredient. In the fragrance, flavor and color trapping systems, encapsulation is used to either delay the release of the particular fragrance or to prohibit an unpleasant odor. With the aspect to polymer encapsulated inorganic particles, it can be broadly applied in filler plastics, packaging, inks, painting and coating. In general, Benefits can be achieved from encapsulation especially in plastics or emulsion paints [33, 6], for example:

- Better particle dispersion in the polymeric matrix
- Improved mechanical properties
- Improved effectiveness in light scattering in a paint film
- Protection of filler or pigment from outside influences
- Protection of the matrix polymer from interaction with the pigment
- Improved barrier properties of a paint film

Several publications review the methods to produce the materials with a micro- or nano- encapsulation structure. For example, Huai et al. [47] reviewed the polymer shell microcapsules with liquid cores, which had been widely used in a variety of industries from food and flavor protection to inkless paper. The methods to form polymer microcapsules include colloidsome formation, polymer precipitation by phase separation, polycondensation interfacial polymerization, layer-by-layer polyeletrolyte deposition, polymer growth by surface polymerization and copolymer vesicle formation. Chavez et al. [22] illustrated a short review of encapsulation in sub-micron species and an alternate strategy for dye encapsulation. In this paper, they focused on several key synthetic approaches to obtain a sub-micron encapsulation structure such as dendritic architectures, hollow particles by polymerization and microemulsions. In a dendrimers, the active molecules can be encapsulated as a core at the beginning of the synthesis or can be incorporated after synthesis. The method to synthesize hollow particles is based on the synthesis of core-shell structure first, then the removal of core materials such as evaporated solution. Microemulsion systems in this paper show the ability to enhance the solubility of active agents in aqueous solutions. Zhong et. al. [124] demonstrated that the tailoring of nanoparticles supported on oxides, dispersed in dendrimers and encapsulated in monolayer shells could lead to novel catalytic applications, which could in general be developed into aggregation- and poison-resistant catalysts of high catalytic activities. Burns [17] reviewed the fluorescent core-shell nanoparticles and these core-shell nanoparticles were synthesized by the inclusion of covalently-bound organic dyes by using sol-gel derived silica as host materials.

Although water-based polymer nanoclay composite can be synthesized by a variety of aforementioned methods, most of these methods are difficult to obtain a core-shell structure in a nanoscale. For example, conventional emulsion polymerization is difficult to locate the dominant polymerization loci at the surface of the inorganic

particles. Miniemulsion polymerization presents as an advantageous encapsulation method because the inorganic particles can be directly dispersed in the monomer droplets and then polymerized on the surface of the inorganic material to form encapsulated upon polymerization. Bechthold et al. [12] coated 120nm $CaCO_3$ particles with a layer of stearic acid by pre-dispersing 5% of these particles in a mixture of styrene and hexadecane. The resulting dispersion was dispersed in water (20% solid) and polymerized. No free $CaCO_3$ was observed by TEM, but pure polystyrene particles were detected. Tiarks F [105] and other researches studied the encapsulation of carbon black by miniemulsion polymerization and the results showed that under optimal conditions, completely coated hybrid particles with up to $80wt.\%$ carbon black and size of approximately 120nm can be obtained. Erdem et al [33] prepared aqueous miniemulsions of styrene containing TiO_2 dispersed particles by both sonication and high-pressure homogenizer (Microfluidizer). Sodium lauryl sulfate was used as surfactant and hexadecane plus polystyrene were acted as the costabilizer. Finally, the maximum encapsulation efficiencies (83% TiO_2 and 73% polystyrene) were achieved using hydrophilic TiO_2 particles stabilized with $1.0wt.\%$ OLOA370. The formation and application of polymer hybrid particles comprising polymeric and magnetic material are of great interest for biomedical application. Recent work shows that the miniemulsion process allows the encapsulation of hydrophilic magnetite. Magnetite particles were capsulated in a polystyrene matrix by a miniemulsion polymerization process [57]. Zhang et. al. [122] synthesized a mono-dispersed silica-polymer core-shell microsphere via surface grafting and emulsion polymerization. Zhang et. al [123] synthesized SiO_2/polystyrene nanocopmosite particles via miniemulsion polymerization by using sodium lauryl sulfate surfactant (SLS), hexadecane costabilizer in the presence of silica particles coated with methacryloxy (propyl) trimethoxysilane. Herreta et. al. [46] obtained aqueous dispersions of silane-functionalized laponite clay platelets. The clay platelets were found to cover the latex surface, giving a faceted

appearance to the particles. However, until now the stable latex of the encapsulated nanoclay inside polymer shell by miniemulsion or emulsion polymerization has not been successfully synthesized yet.

2.4.2 Synthesis of polymer nanocomposite with an asymmetric structure

Self-assembly technology makes it possible by allowing materials to be designed with a hierarchical order and complexity. Theoretical works have shown that anisotropic particles could be very helpful for molecular recognition and self-assembling processes. In present, the synthesis of non-spherical nanoparticles have been extensively investigated. The functionalised hemispheres can recognize themselves by containing the different function groups from left to right, or top to bottom. In 1991, De Gennes was one of the first scientist to use the term Janus for the description of particles whose surfaces are both hemisphere and appear a different chemistry. During the last decade, the "Janus" has been used for describing asymmetric dendritic macromolecules or unimolecular micelles and nanoparticles. Based on the asymmetry from the point view of chemistry, Bicompartmental, dumbbell-like, snowman-like, acorn-like and half-raspberry-like particles were also included into asymmetric particle groups as shown in Figure 12 [86].

Asymmetric particles have very promising applications. Firstly, the amphiphilic particles combining hydrophilic and hydrophobic hemisphere could be very useful for the stabilization of emulsion. Secondly, the asymmetric particles with both negative and positive hemispheres can function as a field polarity, such as the electronic reusable paper. Finally, the asymmetric particles hanging the different chemical groups have the toposelectivity. Therefore, they can be used as bifunctional carriers for catalysis, sensing, drug delivery etc.

Over the last five years, there has been an increasing interest in synthesis of particles or microbeads with non-spherical or asymmetrical spherical shapes [85].

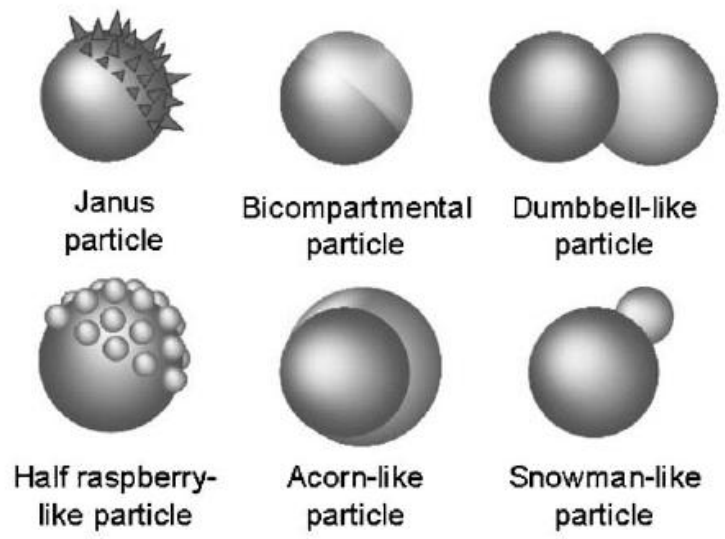


Figure 12: Schematic representation of Janus and comparable particles [86]

Asymmetric particles can be synthesized by chemical and physical methods. Particles with an asymmetric shape could be used as anisotropic building blocks for the construction of advanced materials. Physical methods such as capillary liquid break-up [76], microfabrication [72], and uniaxial stretching of spherical polymer beads [66] are developed to prepare asymmetrical particles. However, these methods are complex because they require unique technology and special substrates and facilities. Furthermore, the particle size is usually in micrometer-scale but not in nanometer-scale. Chemical methods for synthesizing unsymmetrical particles with different morphologies, such as core shell [123], hemispherical [82], and bowl shape [63] are usually prepared via a seeded dispersion or emulsion polymerization approach. Du et. al. [31, 30] prepared poly (methyl methaacrylate-co-styrene) composite lattices with a asymmetric structure by thermally initiated seed emulsion (co) polymerization of styrene, methylmethacrylate (MMA), or styrene and MMA employing a PS or PMMA seed in the absence of conventional initiators. They also synthesized Poly (2-hydroxylethyl methacrylate-co-methyl methacrylate)/ poly (styrene-co-glycidyl methacrylate) (P(HEMA-MMA)/P(St-GMA) composite polymer particles

including two different functional hemispheres by soap-free seeded emulsion polymerization. Their objective of the above work is to synthesize hemispherical nanosphere with different functional groups on either side, which can be stage-modified with chemical and biological nanosystems. Moreover, the hetero-bifunctional nanoparticles have been designed as an enzyme immobilization carrier by cationic hetero-bifunctional poly (glycidyl methacrylate-co-divinylbenzene) polystyrene [P(GMA-DVB)/PS] composite latex. The hydroxyl groups on one side (the PS domain) of the latex beads were bonded to biotin which can specifically bind to the streptavidin template, and the epoxy group on the other side [the P(GMA-DVB)domain] was used to covalently immobilize pyruvate kinase [29]. Several researches [43, 2] prepared the composite micron and submicron-sized polymer particles with different morphologies by seeded dispersion or emulsion polymerization. By controlling the polymerization process variables, seeded dispersion or emulsion polymerization can produce structured latexes exhibiting a wide variety of particle morphologies such as core-shell, hemispherical, or inverted core-shell particles. The mechanism of producing various morphologies is based on the heterogeneous structures generated by the phase separation of the different polymers in the particles during polymerization. Two types of factors concomitantly play an important role in the system. Thermodynamic factors determine the equilibrium morphology of the final composite latex particles, and kinetic factors determine the ease with which the thermodynamically favored equilibrium morphology can be achieved.

CHAPTER III

PROBLEM ANALYSIS AND OBJECTIVES

As reviewed in chapter II, polymer nanoclay composite has a broad range of applications. A uniform dispersion of the intercalated or the exfoliated nanoclay layer into polymer matrix can dramatically improve the composite properties in almost all of the mechanical strength, thermal stability, and barrier properties. Encapsulation of the nanoclay inside polymer particles is one of the viable approaches for a uniform dispersion of nanoclay platelet into the polymer matrix and meanwhile for the protection of solid materials from outside influences. However, although many different polymer-inorganic composites have been extensively investigated recently, polymer encapsulated nanoclay composites in a stable water dispersion have not been successfully synthesized. In this thesis, we seek a feasible approach to synthesize a stable water-based suspension of polymer encapsulated nanoclay composites with an intercalated or exfoliated nanoclay structure. The synthesis approach, the morphology controlling, the polymerization mechanism and the properties improvement have also been extensively studied. It is valuable to mention that miniemulsion polymerization will be served as the primary synthesis approach because of its unique properties reviewed in chapter 2. Therefore, the objectives of this research are:

- to synthesize a stable water-based latex of polystyrene encapsulated nanoclay composite
- to study the impact of reaction conditions on final latex stability, encapsulation degree and the intercalation or exfoliation degree of nanoclay

- to elucidate the effect of nanoclay on styrene miniemulsion polymerization kinetics
- to ascertain the impact of nanoclay on the properties of polystyrene(PS) and polystyrene butylacrylate (PSBA) copolymer films

3.1 Objectives

3.1.1 The synthesis of a stable water-based latex of polystyrene encapsulated nanoclay composite

The stability of the miniemulsion containing nanoclay can be affected by many factors such as the nanoclay particle size and its distribution, the nanoclay content, surface chemistry of nanoclay, the emusification device and polymerization conditions. In this research, all these factors need to be optimized to synthesize a stable water-based latex. Encapsulation is determined by emulsion stability, the interaction of nanoclay and polymer, and the particle sizes of polymer and nanoclay particles. A stable miniemulsion is prerequisite to obtain polymer encapsulated nanoclay composite particles. An instable miniemulsion leads to large composite aggregates containing micro-sized clay, not individual particles with nanoclay platelet inside. Further, the poor interaction of polymer and the clay results in the separation of the clay from polymer matrix. At last, the latex particle size should be large enough to encapsulate the nanoclay platelet inside. In general, the particle size of the clay, the correct surface chemistry of nanoclay and the polymerization conditions play important roles on obtaining both a stable suspension and polymer encapsulated nanoclay.

3.1.2 The impact of reaction conditions on final latex stability, encapsulation degree and the intercalation or exfoliation degree of nanoclay

As reviewed in chapter 2, the higher of the degree of clay intercalation (exfoliation), the greater improvement can be achieved for polymer nanoclay hybrid. Therefore, it is important to know how the reaction conditions affect the efficiency of intercalation

and exfoliation of nanoclay. Moreover, reaction conditions such as the amount of hydrophobe, the stability of miniemulsion before polymerization, the type of initiator, have influence on the latex stability and encapsulation degree, which also need to be investigated in detail.

3.1.3 The fundamental understanding of the impact of nanoclay on the styrene miniemulsion polymerization kinetics

In aspects of polymerization kinetics in the presence of inorganic particles, the conflicted opinions were reported in different publications. Some researcher claimed that inorganic particles do not affect the polymerization kinetics. Others reported that nanoclay has a hindered effect on the polymerization rate. It is important to elucidate the impact of nanoclay on the hybrid styrene miniemulsion polymerization kinetics.

3.1.4 The impact of nanoclay on the properties of polystyrene(PS) and polystyrene butylacrylate (PSBA) copolymer films

After we successfully synthesize a stable water-based suspension of polymer nanoclay composite, the impact of nanoclay on the properties of polystyrene and polystyrene-based copolymer nanoclay composites will be examined. How the inclusion of nanoclay and its loading levels affect the mechanical and thermal properties of the composite films will be ascertained.

3.2 Approach determination

The primary goal of this research is to synthesize a stable water-based suspension of polymer encapsulated nanoclay composites. The surface chemistry of nanoclay and the synthesis approach, which will be discussed in this subsection, are critical to achieve this goal.

3.2.1 Surface modification of clay

The smectite clays have a lamellar structure comprising the repeated layers of two silica tetrahedral layers and an octahedral metal oxide layer. The exchangeable hydrated cations located between the layers facilitate the cation surfactant or the organic monomer or polymer to insert into the layer in order to open the galleries of clays and form an expecting intercalated or exfoliated structure as shown in Figure 13. The clay must be modified from hydrophilic to organophilic to provide a good compatibility between polymer and the clay. Three methods are proposed for the surface functionalization of the nanoclay. One approach is to directly modify the clay by a cationic ammonium surfactant from organophobic to organophilic and then well disperse into the monomer. The second approach is to graft the clay surface by a surface-active monomer, which renders polymerization to grow on the nanoclay surface. Finally, clay is surface grafted by an initiator, which initiates polymerization on the nanoclay surface. However, this initiator grafting method is easier to lose their activity during the modification process and the clay is not intercalated or exfoliated. Therefore, the third approach has not been extensively investigated in this research. In this dissertation, cationic ammonium surfactants with different length of carbon chain, such as: meristyltrimethylammonium bromide (MTAB), cetyltrimethylammonium bromide (CTAB), octadecyltrimethylammonium bromide (OTAB) serve as the ideal surfactants to produce both organophilic and the intercalated clay. Furthermore, instead of these popular ammonium cationic surfactants, a specific surfactant, VBTAC, will act as the modifier for better compatibility of polymer and organoclay. The double bond in its one end reacts with the monomer styrene and the other end adsorbs on the surface of the clay by a ionic bond.

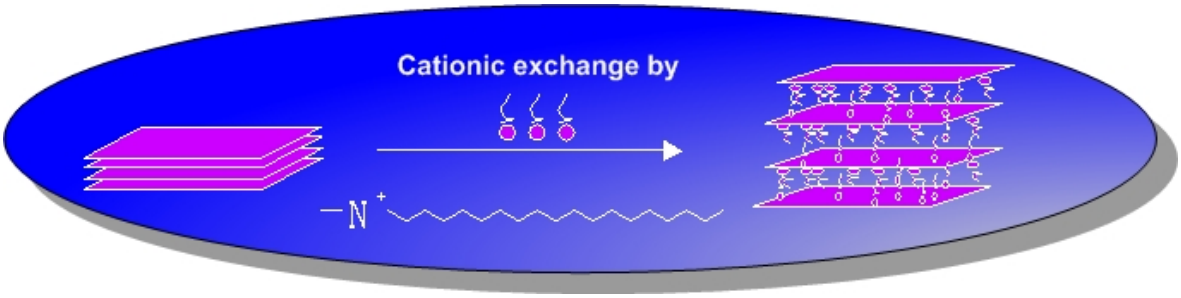


Figure 13: The sketch of clay surface modification

3.2.2 Sythesis method determination

As reviewed in chapter II, traditional emulsion polymerization and miniemulsion polymerization are feasible approaches to form a stable submicron water-based dispersions. The mechanisms of traditional emulsion and miniemulsion polymerizations are compared as shown in the Figure 14 in order to synthesize a stable aqueous suspension of polymer encapsulated nanoclay composites. In conventional emulsion polymerization, the site of polymerization is not the monomer droplets but in the micelles. The micelles are the dominating reaction site. Even though the nanoclay is pre-dispersed inside the monomer droplets, the polymerization on the surface of nanoclay in the monomer droplets does not compete effectively with micelles in capturing the radials because the monomer droplets are not the primary nucleation droplets. As polymerization proceeds, the micelles grow by the addition of the monomer from the water phase. The monomer transfers from monomer droplets with nanoclay inside to micelles or new-initiated polymer particles. The competition between these mechanisms results in polymer particles containing no nanoclay particles and unencapsulated particles. However, in miniemulsion polymerization, the costabilizer acts as an osmotic agent that stabilizes the system against ostwald ripening and retards the monomer outside the droplet. If the water-soluble initiator is used, the polymerization starts from the water phase, whose mechanism is similar as the emulsion polymerization

mechanism. If the oil-soluble initiator is used, in contrast to conventional emulsion polymerization, the droplets themselves are the loci of nucleation. In an ideal miniemulsion polymerization, every droplet behaves as an independent reaction vessel and 1:1 copy of particles occurs. As a consequence, miniemulsion polymerization is believed to be an effective way to produce a stable water-based suspension and polymer encapsulated nanoclay inside the particle is expected.

In summary, two types of surfactants are applied to modify the clay surface in this research. They are cationic ammonium surfactant with a longest carbon chain, OTAB, and the monomer active surfactant, VBTAC. Miniemulsion polymerization serves as the approach to synthesize a stable water-based suspension of polymer encapsulate nanoclay composites because of its excellent stability both before and after polymerization, the submicron droplet size between 50-500 nm, and the unique droplet nucleation mechanism during polymerization. It is worth mentioning that the oil initiator AIBN act as the initiator to further reinforce the particle nucleation during the miniemulsion polymerization process.

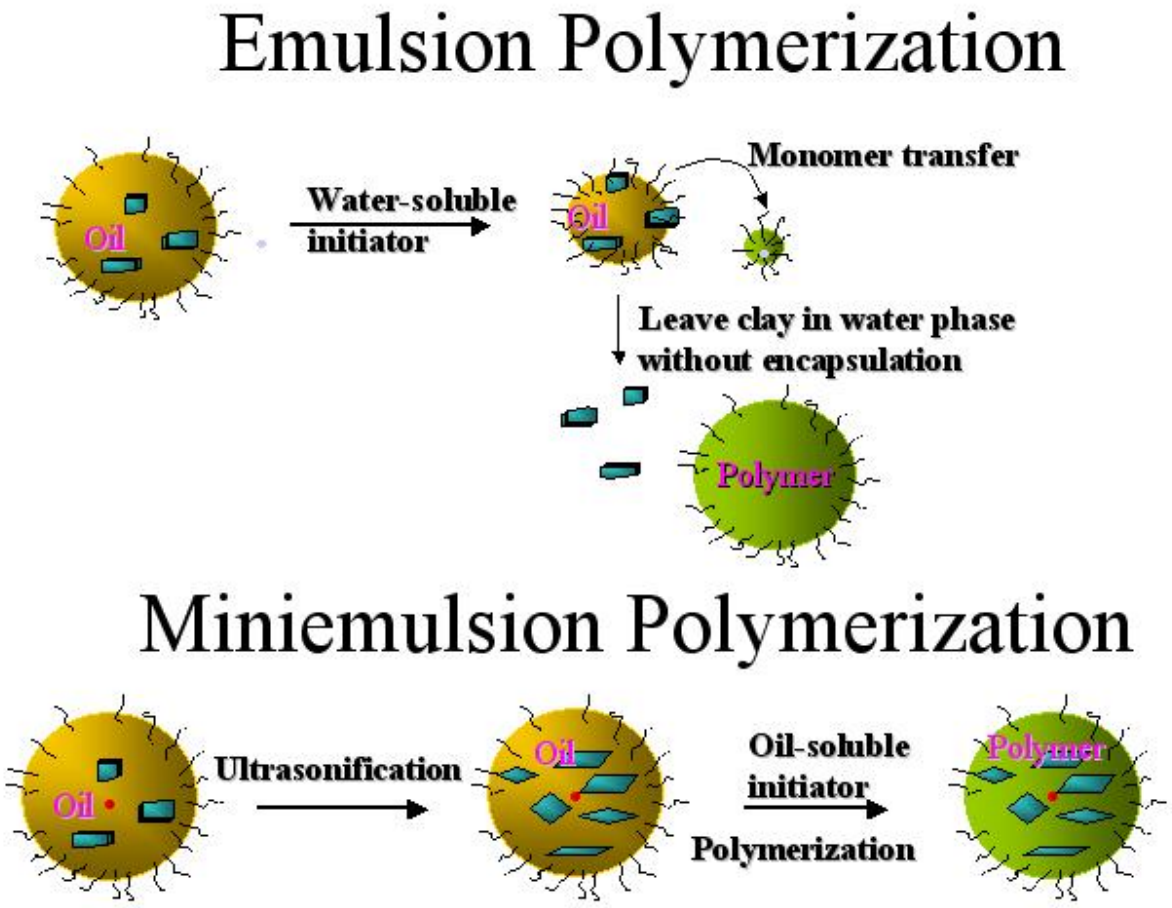


Figure 14: Approach for synthesis by radical miniemulsion polymerization using oil soluble initiator

CHAPTER IV

THE APPROACHES SCREENING TO SYNTHESIZE A STABLE WATER-BASED SUSPENSION OF POLYMER MMT-KSF COMPOSITE

It has been known from the literature review that the effective methods for synthesis of suspension of polymer encapsulated nanoclay composite has been developed. Therefore, the first part of this research is to screen the approaches to achieve the primary three objectives 1), to obtain a stable water-based suspension, 2) to prepare polymer encapsulated nanoclay composite in a water suspension form, and 3) to develop a composite containing the intercalated or exforliated nanoclay. It is believed that three components play a critical role: the type of clay, the surface modification of the clay and the synthesis method. First, by thorough consideration of the cost, the accessibility, cationic exchange capability (CEC) and the particle size, MMT-KSF, which has the average particle size of 450 nm and the CEC of 80-150 milliequivalents/100 grams, was selected as the clay in all preliminary research discussed in this chapter. Second, MMT-KSF was pre-modified in different ways before polymerization. Third, miniemulsion polymerization, which presents advantages as an encapsulated method due to its dominate particle nucleation mechanism and its ability to produce a stable latex due to its submicron particle size, was considered as the primary polymerization approach. Except conventional miniemulsion polymerization, both high solid miniemulsion polymerization and miniemulsion polymerization in the

presence of initiator-grafting clay were investigated in order to improve the interaction of the clay and the organic phase. The emulsion polymerization and seeded emulsion polymerization methods were also under investigation after all the miniemulsion polymerization methods failed to produce a stable water-based suspension. However, with all these efforts, no stable water-based suspension can be achieved via miniemulsion or emulsion polymerization by using MMT-KSF as the clay because of its large particle size.

4.1 Introduction

The methods to synthesize polymer nanoclay composite in non-aqueous phase include monomer intercalation, monomer modification, common solvent, and polymer melt intercalation method [87]. However, suspension polymerization, emulsion polymerization and miniemulsion polymerization are possible polymerization approaches to produce polymer nanoclay composite in an aqueous phase. There are several publications demonstrating how to synthesize polymer nanoclay composite in the aqueous phase via suspension polymerization. Bakhshaee et. al. encapsulated carbon blacks into polystyrene copolymer beads via suspension polymerization [10]. Their results showed that it was possible to produce copolymer beads containing a high yield of carbon black from a wide variety of vinyl monomers and a broad range of carbon blacks. Yeum and Deng successfully synthesized high molecular weight poly (methyl methacrylate)/silver nanocomposite microspheres with a golf-ball morphology by suspension polymerization [119]. Furthermore, Wu et al., Hwu et al. and Gong et al. prepared polymer/MMT nanocomposites by suspension or suspension condensation polymerization and investigated their morphologies and mechanical properties [116, 40]. Their research demonstrated that MMT could be partially exfoliated or intercalated into polymer particles where the polymer nanoclay composites exhibited higher tensile strength and modulus and greater fracture toughness in comparison to

pure polymer(poly[vinyl acetate chloride], PVAC).

A water-based suspension of polymer nanoclay composite was also synthesized via emulsion polymerization. Tong et. al. produced poly (ethyl acrylate)/bentonite nannocomposites by in-situ emulsion polymerization in aqueous dispersions containing bentonite [106]. The transparent nanocomposite film was prepared through direct-forming films of the resultant emulsion. The barrier and mechanical properties of materials were improved dramatically. PMMA nanoclay composites were prepared by in-situ emulsion polymerization and the layered silicates (Gelwhite GP), laponite XLS and MMT, were introduced by either directly adding the unmodified clay in a post polymerization step or by dispersing organophilic modified MMT into the monomer before polymerization [48, 37]. There is numerous research discussing how to encapsulate inorganic particles into polymer shell via minemulsion polymerization. Several publications show that $CaCO_3$, SiO_2, and TiO_2 could be successfully encapsulated by polymer via miniemulsion polymerization [12, 32, 123].

Although the polymer nanoclay composite in an aqueous phase has been reported in previous research. To the best of our knowledge, the stable water-based latex of polymer encapsulated nanoclay composite has not been successfully synthesized. Therefore, in this chapter, we investigate several approaches in attempt to synthesize polymer encapsulated MMT nanocomposite in a stable water-based dispersion. To begin with, MMT-KSF was selected as the nanoclay used for the feasibility study based on the following reasons. Firstly, from the smectite clay family, MMT has the largest cation-exchange capacity of 80-150 milliequivalents/100 grams, which is expected to achieve better coverage on the surface of the clay. Secondly, MMT is very accessible because it has been widely used in recent research. Finally, the MMT-KSF has a suitable particle size of 450nm, which can be encapsulated inside the miniemulsion latex particle with the particle size in the range of 50-500nm. At last, MMT is very cheap in comparison to other smectite clays such as laponite.

In summary, a list of emulsion and miniemulsion polymerization methods were applied to synthesize a stable water-based suspension of polymer nanoclay composite as follows.

- Miniemulsion polymerization
- High solid miniemulsion polymerization
- Miniemulsion polymerization with an initiator-modified clay
- Emulsion polymerization with ionic surfactant and the acid monomer
- Seeded emulsion polymerization

4.2 Experiment, Result and Discussion

4.2.1 Materials

MMT-KSF was provided by Southern Clay Products INC. The plate is about 450 nm (measured by TEM). NSC was purchased from "The Source Clays Repository", University of Missouri. Oil soluble initiator, 2, 2'-Azoisobutyronitrile (AIBN) was a product of Waco Chemicals USA, Inc. Hexadecane (99%), styrene (99%), meristyltrimethylammonium bromide (MTAB), cetyltrimethylammonium bromide (CTAB), octadecyltrimethylammonium bromide (OTAB), sodium laurel sulfate(SLS), Triton 405 (TX-405,

$$4 - (C_8H_{17})C_6H_4(OCH_2CH_2)_{40}OH,$$

70% solution in water), (ar-vinylbenzyl) trimethylammonium chloride (VBTAC, 99%), molybdenum hexacarbonyl and ammonium persulfate(APS) were purchased from Aldrich Chemical Inc. The styrene and butyl acrylate (BA) monomers were purified by washing with 5 wt.% NaOH solution followed by de-ionized water until pH of 7, and then was distilled under reduced pressure and stored in the refrigerator prior to use. Methacrylic acid was distilled with reduced presure and stored in the refrigerator prior to use. All other reagents were used as received.

4.2.2 Miniemulsion polymerization

The direct dispersion of the clay into the oil phase, oil-soluble initiator and the characteristic features of the miniemulsion polymerization technique, are expected to provide potential advantages for the encapsulation of nano-clay inside polymer particles. Furthermore, if nanoclay is well-dispersed into polymer particles, a stable suspension should be obtained as well. According to previous research [12, 32, 123], in miniemulsion polymerization, a stable miniemulsion before polymerization is prerequisite to form a stable miniemulsion after polymerization. Therefore, many different processes have been conducted to form a stable miniemulsion before polymerization. To begin with, the hydrophilic MMT-KSF and the cationic surfactant CTAB was directly added into the monomer and the ultrasonification was conducted to form a uniform dispersion of oil-clay mixture. As a result, the clay was precipitated out and separated from the styrene monomer. The results suggest that in order to uniformly disperse MMT-KSF in the styrene monomer, the clay must be converted from hydrophilic (water-like) to organophilic (oil-like). For this reason, the MMT-KSF was modified by a cationic surfactant with different carbon chain OTAB (18 carbon chain), CTAB(16 carbon chain) and MTAB (14 carbon chain). The (X-ray diffraction)XRD patterns show that the OTAB modified MMT-KSF has the largest intercalation degree. Then this modified clay was dispersed into the styrene monomer and conducted by ultrasonification. Meanwhile, the co-stabilizer (hexadecane) and the oil-soluble initiator AIBN were also introduced in the oil phase. After ultrasonification, the uniform dispersion of oil-clay mixture was formed. Then this oil phase was dispersed in the aqueous phase containing water and surfactant Triton-405 under a vigorous mechanical stirring and a ultra-sonification to form the miniemulsion before polymerization. We found that a thin layer of oil phase floated on the resultant emulsion and if it sat for several hours, the clay precipitated out onto the bottom from the emulsion phase. If immediately miniemulsion was conducted at 70 ^{o}C under nitrogen purge, no stable

water-based suspension was produced. Even though the complex miniemulsion polymerization parameters were optimized, such as the ultrasonification and mechanical stirring conditions, the loading level of surfactant and hydrophobe, in combination of ionic surfactant SLS and non-ionic surfactant TX-405, a stable emulsion before and after polymerization was not produced. The clay was precipitated on the bottom after polymerization and the phase separation was observed after emusification. The reasons are probably attributed to the high density and the large particle size of KSF-MMT, or the poor interaction between the clay and the organic monomer, which leads to the phase separation of miniemulsions before polymerization. Therefore, the following approaches focus on how to manipulate the larger emulsion droplets in order to encapsulate the large clay particles, improve the interaction between the clay and the organic phase, and sustain the high-density clay particles in the emulsion phase by increasing the oil-phase viscosity.

4.2.3 High solid miniemulsion polymerization

We introduced a high solid miniemulsion polymerization method in order to resolve the problems due to high density of MMT. The high-density clay particles were expected to sustain in the creamy phase by increasing miniemulsion viscosity. The solid content of the miniemulsion was increased from 60% to 80% according to the solid content shown in previous reseach [1], where the creaming phase could be formed when the solid content of miniemulsion was larger than 60%. Moreover, the latex with high solid content has other advantages, i.e, lower shipping costs and less water removal. The procedure is similiar to the aforementioned miniemulsion polymerization method. The miniemulsion before polymerization was emulsified under a high mechanical force (stirring speed as high as 20,000 rpm) for 10 minutes, and sodium dodecyl sulfate (SDS) was added as a co-surfactant with Triton-405. The results show

that final latex was stable without the precipitation of the clay for several hours. However, after a few days, the clay precipitated out. It indicates that the clay was only sustained by the high-viscosity creaming phase, but not adhered on polymer particles. Figure 15 shows morphologies of final latex particles via high-solid miniemulsion polymerization and it demonstrates that the aggregates were formed in final latex and no individual particles can be recognized. By exploring high solid miniemulsion polymerization, we also tested the influence of two kinds of initiators, namely, the oil-soluble initiator AIBN and the water-soluble initiator APS, on the stability of the miniemulsion. It was found that in final latex, the precipitates obtained by centrifugation contained more clay when a water-soluble initiator was used in comparison with that of an oil-soluble initiator. This suggests that more clay particles were associated with polystyrene droplets when an oil initiator was used. These results also indicate that a small amount of nanoclay could be associated with polymer particles via high solid miniemulsion polymerization and the oil soluble initiator faciliated this association. This can be explained by the following two reasons, respectively. Firstly, a small number of clay with a small particle size could be associated with polymer particles. Secondly, the oil soluble initiator aids the particle nucleation and the nanoclay could stay inside the particles without monomer transferring from the oil droplets.

4.2.4 Miniemulsion polymerization with initiator grafting on the clay surface

Both miniemulsion and high-solid miniemulsion polymerization could not produce a stable water-based suspension of polymer nanoclay composite because the poor interaction of the nanoclay with the organic phase. The surface grafting of initiator on MMT-KSF clay surface was studied in order to initiate the polymerization on the surface of nanoclay. Following the similar procedure of miniemulsion aforementioned, trichloroacetyl groups were introduced onto KSF particle surface, and then

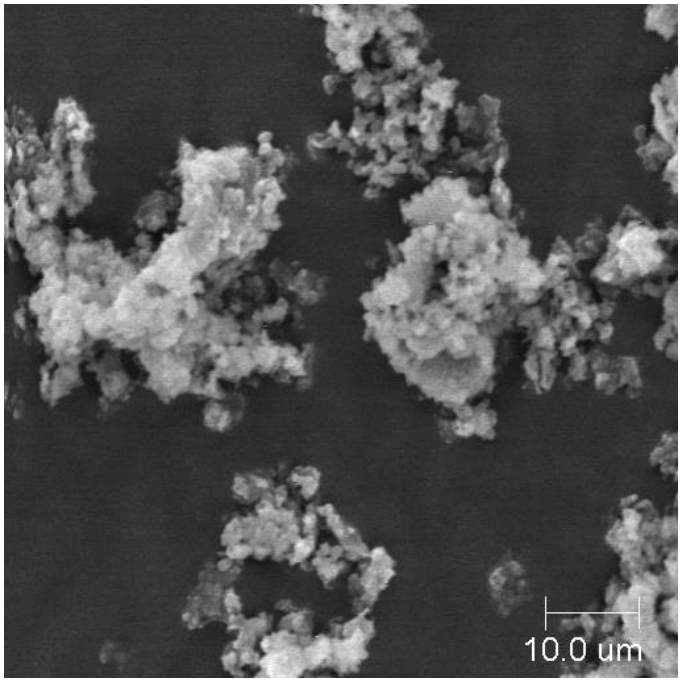


Figure 15: TEM image of polystyrene nanoclay composite via high solid miniemulsion polymerization

miniemulsion polymerization of styrene was processed using molybdenum hexacarbonyl ($Mo(CO)_6$) as the initiator. The reactions are shown as follows in the two equations in Figure 16. The results show that final latex comprised the muddy polymer with a very low molecular weight and a low conversion (lower than 60%) of polystyrene and the precipitated clay, which sat on the bottom of the reactor after polymerization. The experiment failed to form a stable latex.

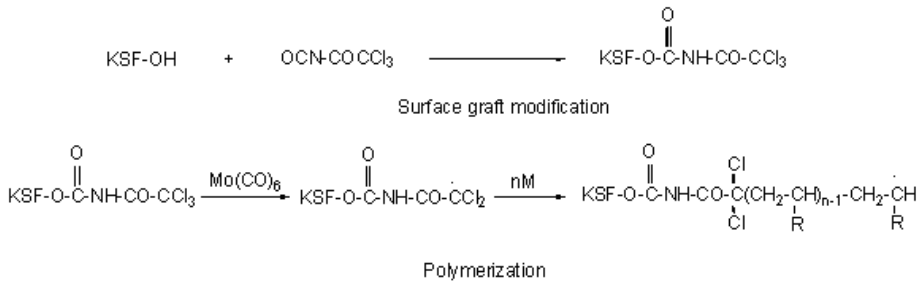


Figure 16: Graft reaction

In summary, miniemulsion polymerization, high solid miniemulsion polymerization, and miniemulsion polymerization in combination with surface modification of

nanoclay by an initiator have not successfully produced a stable miniemulsion before and after polymerization. The particle size of miniemulsion was considered as critical to stability of the system. Therefore, the particle size of supernatant was measured by light scattering and the result shows that the particle size of supernatant was less than 200 nm. However, the average particle size of MMT-KSF is about 450 nm and has a broad distribution (from 100 nm to 1 μm). It is clear that the small polymer particles could not encapsulate the clay with a larger particle size and as a result, clay could not associate with polymer particles and it separated from polymer particles during polymerization. Therefore, conventional emulsion polymerization and seeded emulsion polymerization were explored to form larger polymer particles to encapsulate the larger clay particles.

4.2.5 Conventional emulsion polymerization

Dong-Guk Yu et al. [121] reported that titanium dioxide core/polymer shell hybrid composite particles were successfully synthesized by emulsion polymerization. In this study, a similar method was applied to encapsulate the clay particles into polymer. Emulsifiers (SLS and Triton X-100) and unmodified MMT-KSF dispersed in the aqueous phase were introduced into the reaction flask, heated to 70 ^{o}C, and then stirred at a rate of 250 rpm under bubbled nitrogen gas. After 30 minutes, water soluble initiator ammonium persulfate and the monomer mixture were poured into the reaction flask. The pH of the reactant mixture was adjusted by the addition of HCl or NaOH solution. The reaction was then polymerized for 24 hours under a constant stirring rate. poly(methyl methacrylate-co-n-butyl acrylate-comethacrylic acid) [P(MMA-BA-MAA)] were prepared instead of pure polystyrene. The groups in the acid monomer and ionic surfactant SLS were expected to covalently bond with the hydrogen group of hydrophilic MMT-KSF in order to improve the interaction of the

clay with the organic phase. However, although the above method has been successfully applied to synthesize stable and encapsulated TiO_2 inside polymer matrix, this method failed to synthesize a polymer encapsulated clay composite and the clay was precipitated out during emulsion polymerization due to the different morphologies and surface properties of TiO_2 and MMT-KSF.

4.2.6 Seeded emulsion polymerization

The seeded emulsion polymerization with the oil soluble initiator was conducted as well. Firstly, The organophilic surface modified MMT-KSF (with approximately 10% OTAB) was copolymerized with monomer styrene through UV initiated bulk polymerization. Thereafter, the surface modified nano-clay with $10-16\%$ surface coverage of polystyrene was acted as the seed for the following emulsion polymerization. A cationic monomer VBTAC was also introduced into the oil-clay mixture in order to improve the compatibility between the clay and the monomer. The procedure is as follows: Firstly, the MMT-KSF seed and the cationic monomer VBTAC were predispersed in monomer styrene with the addition of the oil soluble initiator AIBN. Thereafter the oil phase was mixed with the water phase (the mixture of D.I water and Titron-405) and magnetically stirred for 30 minutes. Then this mixture was emulsified by ultrasonification for 3 minutes and the emulsion polymerization was conducted at $70\,^{o}$C under a constant stirring rate of 600 rpm and under a nitrogen purge. Unfortunately, phase separation occured after emulsification and the clay was precipitated during polymerization. A starving feeding (styrene in a syringe pump was dropped into the reactor at the speed of 0.5 ml/min during polymerization) was processed in combination with seeded emulsion polymerizaiton, which was expected to make polymerization grow on the surface of seeded inorganic particles. However, the clay was still precipitated out from the emulsion phase during polymerization.

4.3 Conclusion

Through a thorough and time-consuming process of screening a variety of synthesis approaches, a feasible synthesis method to produce a stable water-based suspension of polymer clay nanocomposite by using MMT-KSF as clay was not found in this study. An emulsion via high solid miniemulsion polymerization was stable for several hours because the high-viscosity emulsion could sustain the clay temporarily. However, a long-term stable water-stable suspension of polymer nanoclay composite was not achieved yet. Emulsion polymerization and seeded emulsion polymerization also could not produce a stable water-based suspension and MMT-KSF separated from polymer particles after polymerization. The results indicate that the large particle size(the average particle size of 450 nm) of MMT-KSF as shown in Figure 17 and a diversified particle size distribution (100 nm-several μm) prevent a stable suspension in the aqueous phase. Therefore, the screening of clay varieties with a suitable particle size as candidates for encapsulation is critical to forming a stable latex.

4.4 Recommendation - screening clay varieties

In order to find a clay candidate to achieve our objectives, different clay minerals, such as laponite, saponite, MMT, and Bentonite, were dispersed and observed by TEM. Although laponite has very small particle size of several nanometer and a uniform particle size distribution, it is the most expensive clay, which is not chosen for our system. Bentonite, which has similar properties as MMT, has a larger particle size and a broader particle size distribution than MMT. Therefore, it can not be encapsulated inside polymer particles and form a stable suspension according to the results of MMT in this chapter.

We found that NSC, with the average particle size of 200 nm, as shown in figure 18, may be suit for the production of a stable water-based suspension of polymer nanoclay composite. The further experiment shows that organo-NSC, which is modified with a

certain cationic surfactant, can be well dispersed in the monomer phase. Therefore, NSC will be used as the clay materials in the following experiment in Chapter V.

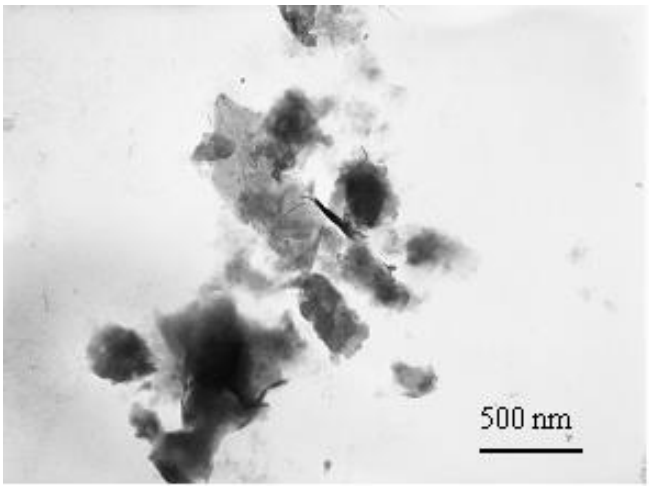


Figure 17: The TEM image of MMT-KSF dispersion in water

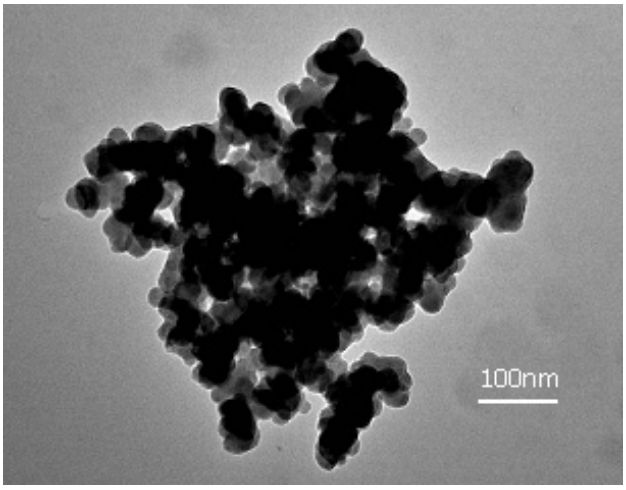


Figure 18: The TEM image of NSC clay dispersion in water

Although all synthesis approaches in this chapter failed to synthesize a stable water-based suspension of polymer encapsulated nanoclay composite, they provided some important information that would be very beneficial for future research. Firstly, it indicates that the particle size and its size distribution of nanoclay is critical to producing a stable aqueous suspension, which is a prerequisite in producing nanocapsule with a core shell structure. Secondly, the surface modification of nanoclay and

the stability of the suspension by dispersing the modified clay in the oil phase before polymerization are prerequisites to forming a stable latex after polymerization. Many approaches tested in these experiments such as surface modification methods, which can improve the interaction of the clay and the monomer, could be applied in our following research. Finally, nanoclay could be intercalated through pre-modification by a cationic surfactant such as OTAB, CTAB, VBTAC.

CHAPTER V

SYNTHESIS OF WATER-BASED POLYSTYRENE-NANOCLAY(NSC) COMPOSITE SUSPENSION VIA MINI-EMULSION POLYMERIZATION

The previous conclusions indicate that the particle size and the surface modification of nanoclay play a critical role on the stability of miniemulsion. If the nanoclay particle size is too large, it can not form a stable suspension in the oil phase, so a stable suspension can not be successfully synthesized. It was also concluded from last chapter that small-sized NSC could form a stable dispersion in the monomer styrene. Therefore, in this chapter, by using NSC with an average particle size of approximately 200 nm, we report the synthesis of a stable water-based polymer nanoclay colloids containing the intercalated clay platelets via miniemulsion polymerization. Meanwhile, the effects of clay modification conditions on the stability of miniemulsion and the optimum conditions for preparing stable emulsion were also investigated. The result show that, although a stable suspension is obtained, the clay NSC is not able to be encapsulated inside the polymer particles because the small-sized latex particles (90-120 nm) can not encapsulate the clay platelets with the average size of 200 nm. The stability of the suspension and the intercalation degree of the clay was strongly affected by the pretreatment of NSC with cationic surfactant OTAB. It was also found that the addition of clay slightly reduced both the reaction rate and the

conversion of miniemulsion polymerization. [1]

5.1 Introduction

Current research for the synthesis of water-based polymer-nanoclay composite is reviewed, which provides background for our study. For example, Xu et al. [117] described a method to synthesize intercalated poly (styrene-co-methyl)/clay nanocomposites through an emulsion polymerization by using reactive surfactant, 2-acrylamide-2-methyl-1-propane sulfonic (AMPS), which was claimed to make the polymer end tethered on pristine Na-MMT. Huang and Brittain [48] synthesized the PMMA-layered silicate nanocomposites by suspension polymerization and emulsion polymerization. They simply mixed the unmodified clay into the aqueous phase or added the clay in post-polymerization step. The final products obtained were not thermodynamically stable water-dispersion latex but in form of aggregates. Herrera et al [46] synthesized the water-based polymer/clay nanocomposites by first chemically modifying the laponite clay minerals by the silant agents (-methyacryloxy propyl mono-, di, tri-methyl ethoxysilane) before polymerization and then proceeding with seeded emulsion polymerization. However, the stability of final latex was not reported. Our recent work indicated that a stable nanocomposite suspension can be prepared by encapsulation of laponite in the polymer latex particles [96]. However, when montmorillonite with an average size about 450 nm (SEM estimation) was used as layered silicate particles, the encapsulation is unsuccessful because of the large plate size of the montmorillonite. In this study, intercalated saponite particles with a plate size of 200-300 nm were used and their polymorphs in the final products were studied. Generally, intercalated nano-composite consists of a regular insertion of the host materials between the clay layers, while for the exfoliated nanocomposite, 1 nm-thick

[1] This chapter has been modified from the following publication: synthesis of water-based polystyrene-nanoclay composite suspension via miniemulsion polymerization, Industrial and Engineering Chemistry Research, 2006, vol.45, n8, page 2641-2645.

layers are dispersed in the matrix and the host layers have lost their entire registry [20].

Miniemulsion polymerization is an effective way to obtain thermodynamically stable water dispersion. Miniemulsion is specially formulated as a heterophase system where stable nanodroplets are dispersed in a continuous phase. Miniemulsion is usually more stable than similar conventional emulsion and is able to be used for preparation of latex suspension with the particle size between 50-500 nm with a uniform particle distribution [4, 12]. The costabilizer, which generally has high monomer solubility and low water solubility, can significantly suppress the coalescence of droplets and retard the Oswald ripening. In this study, stable polystyrene/nano-saponite composite suspensions were successfully synthesized with optimized polymerization conditions.

Surface hydrophobicity of clay particles is important in miniemulsion polymerization. It has been well known that basal surfaces of clay are hydrophobic, and the edge surfaces are hydrophilic. The hydrophobicity of basal surfaces arises from the fact that the atoms exposed on the surface are linked together by silozane (Si-O-Si) bonds, and hence, do not form strong hydrogen bonds with water. The edge surfaces, on the other hand, are composed of hydroxyl ions, magnesium, silicon and substituted cations, all of which undergo hydrolysis. As a result, the edges are hydrophilic and can form strong hydrogen bonds with water. In most cases, unmodified clay prefers to stay in the water phase or oil-water interface but not in the oil phase. In order to prepare nanoclay containing polystyrene/nanoclay composite suspension, clay must be modified into organophobic particles. Furthermore, the hydrophobicity of basal surfaces is also important in terms of intercalation of clay particles because the hydrophobic basal surfaces aid the entry of monomer into the intergalleries of the clay. The most common method for clay surface modification and intercalation is to treat the clay with cationic surfactant, such as CTAB and OTAB. In this study, the effects

of cationic surfactant on clay distribution in the final products are also investigated.

5.2 Experiment

5.2.1 Materials

Materials refer to chapter 4.

5.2.2 Procedures

Preparation of intercalated organo-clay: A 5 g saponite-Ca was dispersed into water with 5 mmol OTAB and stirred at 50 ^oC for 24 hours. The saponite particles were separated by centrifugation (5000 rpm, 10 minutes) and washed with large amounts of water and ethanol to remove extra (unreacted) OTAB until no bromide can be detected by silver nitrate. The sample was dried in the vacuum oven overnight at 45 ^oC. The dried organo-clay was ground to a powder with the aggregated particle size less than 45 micrometer.

Miniemulsion preparation and polymerization: The miniemulsion preparation conditions are given in Table 5. Oil phase A contains 1.2 g hexadecane (co-stabilizer) and 0.24 g AIBN in 12 g styrene monomer and required saponite (0.25 g or 0.6 g). The mixture was then exposed to 2-minute sonication (W-385 sonicator, Heat System-Ultrasonics Inc., USA). The viscosity of the system increased if the concentration of intercalated saponite was increased. At a clay concentration higher than 5%, gel-like suspensions were obtained. The aqueous phase B was prepared by dissolving 2 g TX-405 in 100 g water at room temperature. The intercalated saponite-styrene mixture A was poured into aqueous phase B, and the mixture was cooled in the ice bath. After vigorous stirring of the mixture in the ice bath for 30 minutes, miniemulsion was made by 3-minute sonication in the ice bath. This miniemulsion was then ready for either property characterization or for subsequent polymerization.

Upon completion of the sonication, the as-prepared miniemulsion was poured into 3-neck flask under bubbling N_2. The miniemulsion was held at room temperature

Table 5: The Basic Recipe for Miniemulsion Polymerization of PS/NSC Nanocomposite Suspension Particles

Component	Amount added (g)	Percentage in total ($wt.\%$)	percentage to monomer ($wt.\%$)
		Mixture A	
styrene	12.0	10.4	100
NSC	$0.48 - 0.6$	$0.2 - 0.5$	$2.0 - 5.0$
Hexadecane	1.2	1.0	10.0
AIBN	0.24	0.2	2.0
		Mixture B	
Tx-405	2.0	1.7	16.7
Water	100.0	86.5	833.3

and degassed for 30 minutes. After degassing, the temperature of the mixture was increased to $70 \pm 2\,^{o}$C, and the polymerization was conducted at this temperature for 6 hours under continuous mechanical stirring at 600 rpm and terminated by dropping one drop of 2% 4-methoxyphenol solution into the latex. Stable suspension was obtained under favored polymerization conditions.

5.2.3 Characterizations

The exchange ability of saponite by OTAB (expressed by meq./100 g) was determined from the weight difference (D_W) of organic clay before and after incineration ($900\,^{o}$C, 2 hours) using the following equation:

$$\text{grafted amount}(mequiv/100g) = \frac{\Delta W \times M_w}{W} \times 10^{-5} \tag{14}$$

W and M_w are the weight of saponite powder after incineration and the molecular weight of OTAB, respectively. The incineration experiments were carried out in an Isotemp Programmable Forced-Draft furnace (Fisher Scientific Inc.).

The stability of the miniemulsion before polymerization was evaluated by sedimentation rate of the suspension in a long test tube. The boundary moving rate between supernatant phase and milky emulsion phase as a function of time was recorded. The

miniemulsion without any phase separation after 24 hours was named as stable suspension. Otherwise, the change rate of the boundary as a function of time in 24 hours was recorded to indicate the stability of the emulsion.

The particle size and polydispersity were carried out on a Malvern zetasizer 3000 at 25 ^{o}C at a fixed angle of 90^o. Before the measurement, the latex was diluted by an aqueous solution containing TX-405 in the same concentration as the mother liquor to reduce the dilution effect on droplet stability.

X-ray powder diffraction patterns were obtained using a PW 1800 x-ray diffractometer (Philips, USA) using Cu, Ka ray ($l = 1.5405^oA$) as the radiation source. A step size of 0.04^oA and a scan step time of 0.5 s were adopted. The d (001) basal-spacing of the clay and intercalated clay were calculated using the Bragg equation:

$$d = \frac{\lambda}{2\sin\theta} \tag{15}$$

A JEOL 100C transmission electron microscope (TEM) at an accelerating voltage of 100 KV and beam current of 70 mA was used to examine clay morphology. The stability of the final suspension was investigated using a Beckman 20 centrifuge at 10,000 rpm for 30 minutes at room temperature. The incineration experiments were carried out in an Isotemp Programmable Forced-Draft furnace at 525 ^{o}C for 5 hours in order to obtain the percentage of clay separating at high speed.

5.3 Result and discussion

5.3.1 Modification and dispersion of NSC

The surface properties of clay play a critical role in the dispersibility of intercalated clay in the monomer. The untreated clay particles are organophobic and not easily dispersible in organo-media. The modification of clay using quaternary ammonium cation not only exfoliates the clay galleries but also converts the clay from organophobic to organophilic so the particles can be dispersed in monomer phase. The 18-carbon atom OTAB, which has been used to form the most stable latex in our previous work

[20], is chosen as the modifier. The actual cationic exchange capacity of NSC using OTAB is 77.32 meq /100g by incineration experiment, which agrees very well with the provided maximum cationic exchange capacity by the clay supplier (75-80 meq /100g). This agreement suggests that the exchange of Ca with OTAB is complete in our experiments and no remarkable amount of free OTAB remains in the system. The OTAB treated saponite was intercalated as evidenced by X-ray diffraction measurement. As shown in Figure 19, the pristine Saponite-Ca has an interlayer spacing of d 1.24 nm corresponding to $2\theta = 7.14^o$ (d 001 reflection), and the surface modified Saponite clay has shifted to $d = 1.92$ nm corresponding to $2\theta = 4.6^o$.

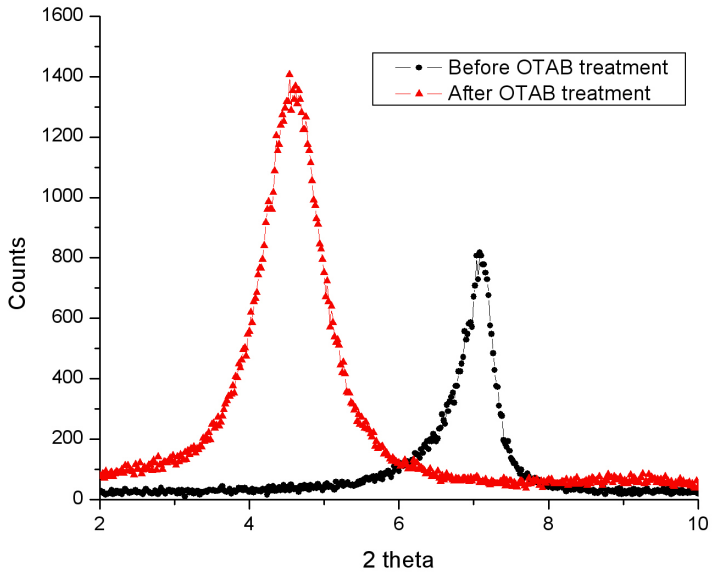


Figure 19: XRD pattern of saponite before and after OTAB treatment

5.3.2 Distribution of the clay in water and oil phase

In order to further understand the surface properties of clay before and after modification, the ratio of pristine and modified clay in oil and water phases was studied. Without the presence of costabilizer hexadecane, the experiment shows that 96% of the surface modified clay stays in the oil phase, while the pristine clay (81%) is

predominantly present in the water phase.

The effect of co-stabilizer and clay concentrations on the distribution of the clay between water and oil phases was also investigated. However, there was no clear tendency observed in the concentration range used in this study. As shown in Figure 20, more than 85% of OTAB-modified clay particles were in the monomer phase in all hexadecane concentrations although the data is scattered. Meanwhile, more than 90% of organo-clay particles were in the monomer phase in the all clay concentrations in the absence of hexadecane co-stabilizer.

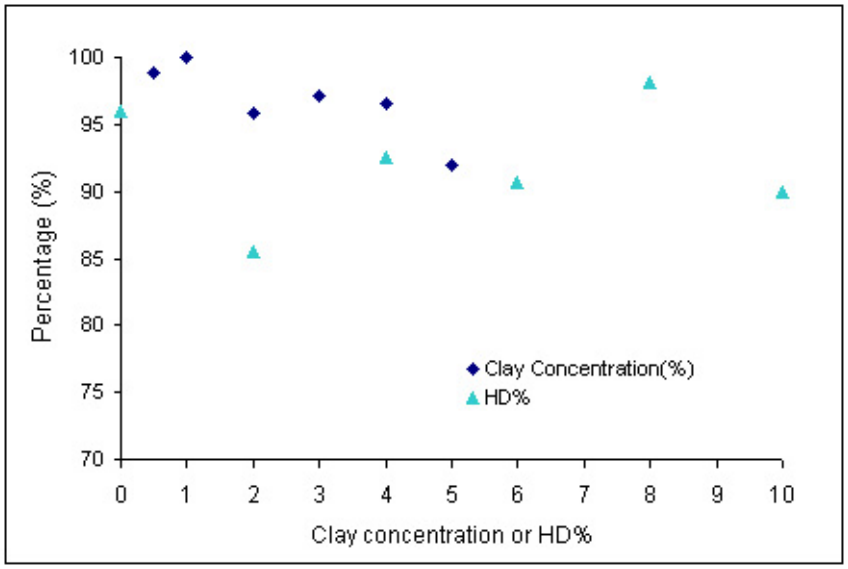


Figure 20: Percentage of organo-clay in the oil and interface as a function of hexadecane (HD) concentration and clay content in the absence of hexadecane co-stabilizer

It is well known that mechanical homogenization is an important step for preparing a stable emulsion or miniemulsion. Ultrasonication has been commonly used to make stable emulsion or miniemulsion. It was found in this study that the ultrasonification treatment is a very important factor in obtaining a stable emulsion. However, because a quantitative study of the ultrasonification effect needs well defined equipment and experimental setup and is beyond the goal of this research, only a qualitative study

was conducted. The results indicated that, at our experimental conditions, the relative high energy import at short ultrasonic time (3 minutes) benefited the formation of stable and uniform emulsion droplets. Increased ultrasonic time beyond 5 minutes will cause a coalescence of the emulsion particles. It was also found that the stability of final nanoclay composite strongly depended on the stability of pre-polymerization miniemulsion. A large precipitated clay-polymer solid mixture was observed when an unstable emulsion was used in the polymerization.

5.3.3 Effect of hexadecane co-stabilizer on the particle size and final latex stability

It has been known that a small amount of hydrophobe builds up an osmotic pressure in miniemulsion droplets which provides stability against oswald ripening. The required minimum molar ratio of hydrophobe to monomer is about 1:250 for creating enough osmotic pressure in the droplets [56, 57, 32]. Responding to the above empirical content, 2-10 wt.% hexadecane based on monomer styrene was used in this study. Although Table 6 shows that the particle size of latex after the polymerization slightly depends on the amount of the hydrophobe, it was found that the hexadecane had large influence on the thermodynamical stability of the final latex. When the hexadecane was increased from 2% to 10% (based on the monomer styrene), the clay particles in the final product were stable and only a very small portion could be separated by ultracentrifugation. This reveals that the hexadecane not only reduced Oswald ripening as conversional miniemulsion did but also acted as a compatibilizer for stabilize intercalated saponite particles in the system.

5.3.4 Effect of nanoclay particles on polymerization conversion

In emulsion polymerization, monomer droplets act as monomer reservoirs to supply the monomer to the growing polymer particles. However, in miniemulsion polymerization, the monomer droplets become the principle locus of particle nucleation, which

Table 6: Effect of hexadecane on final latex stability and particle size

Expt	HD (g)	Particle size	Poly index	Clay in precipitate after centrifugation (%)
HD1	10	97.87	0.173	_[b]
HD2	6	104.5	0.151	35
HD3	2	109.7	0.171	37.5

[a] The Recipe for the other chemicals is shown in Table 5. [b] Unmeasurable

in turn, exhibit different polymerization kinetics and final particle size distributions [99].

The effect of inorganic particles on the polymerization rate and conversion has been studied in the literature [75, 51]. Generally speaking, the addition of inorganic particles, such as SiO_2, TiO_2, $CaCO_3$ and Ag, will reduce both monomer conversion and reaction rate in emulsion and suspension polymerizations. Similar results were obtained in this study. The final conversions after 6 hours polymerization without and with 2% clay are 95% and 85%, respectively. It was concluded from this data and the results shown in Figure 21 that both polymerization rate and maximum conversion degree decreased with the addition of nanoclay in the miniemulsion. It is believed that the reactivity of radicals and living polymers is lower in the presence of clay particles because of the adsorption of these living species by large nanoclay surface. It was also found that the average particle size and polydispersibility of final products slightly increased with the addition of nanoclay.

5.3.5 Characterization morphology and stability of the latex in the presence of pristine saponite or pre-modified saponite

As discussed before, pristine clay particles are organophobic and undispersible in the monomer. It was found in this study that pristine clay particles could be partially dispersed in styrene monomer by ultrasonification, but they precipitated out from the monomer quickly after the ultrasonification was stopped as shown in Figure 22-1(left). However, the organo-saponite clay suspension in the monomer obtained by

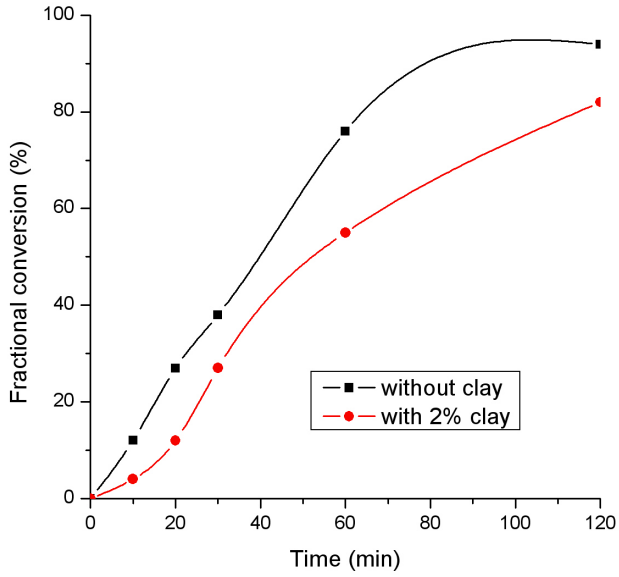


Figure 21: Conversion vs. time without clay and with 2% clay

the ultrasonification treatment in the presence of OTAB was an almost transparent homogeneous solution at a low clay concentration ($< 5.0 wt.\%$). It was also found that OTAB treated clay formed a gel in styrene when the concentration of clay was higher than 5.0 $wt.\%$ as shown in Figure 22-1 (right). The gel formation in the monomer combined with the aforementioned XRD results strongly suggest that the saponite particles were intercalated and well swelled by the monomer.

TEM morphology observations of the final product prepared in the presence of 5% pristine and surface modified (organophilic) clays are illustrated in Figure 22-3. It can be seen that clay particles in the final products are separated from polymer latexes when pristine saponite was used. However, if clay particles are pre-modified with OTAB, nanoclay layers are surrounded and entrapped by latex particles. It is interesting to note that although clay particles in Figure 22-3 are strongly adhered together with latex particles, they are not perfectly encapsulated by the polymer. This is different from our previous study using modified laponite in which nanoclay particles were fully encapsulated by polymer molecules. One of the major differences

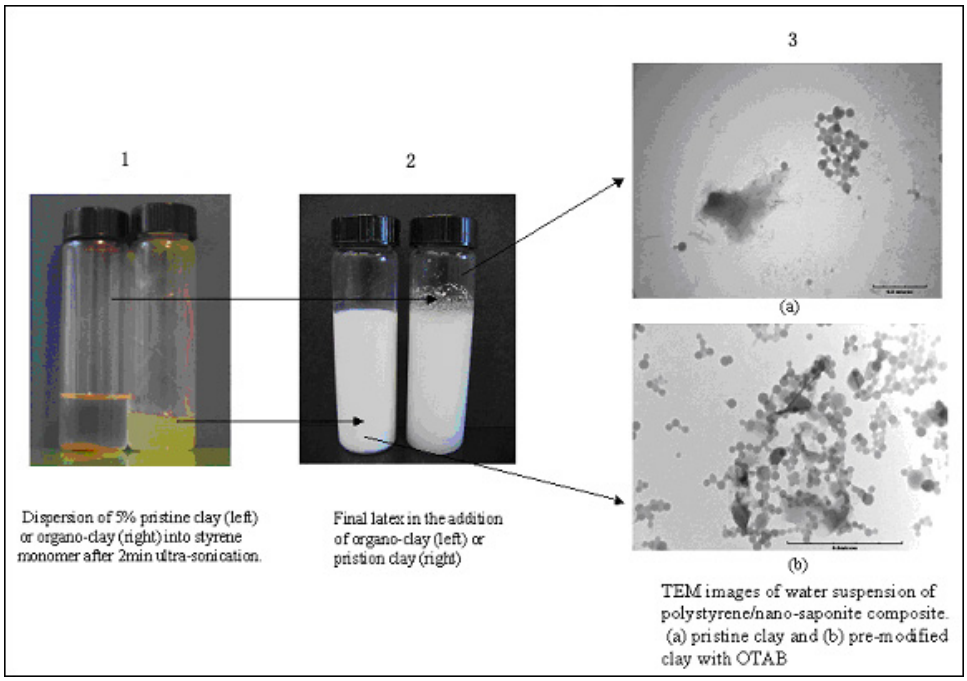


Figure 22: Suspensions before and after polymerization and TEM images of final latex in the addition of pristine clay or pre-modified clay

between the saponite used in this study and the laponite used in our previous research is the particle size. It is well known that miniemulsion is comprised of relatively stable oil droplets with a particle size commonly less than 300 nm. Figure 22-3(b) and Table 6 illustrate that the latex prepared is about 100 nm, which is much smaller than intercalated saponite particle size (about 200-300 nm). Obviously, the large platy nanoclay particles cannot be encapsulated by small latex particles. The effort in preparing large and stable miniemulsion droplets in the presence of nanoclay failed due to the conflict between making stable miniemulsion and increasing the droplet size.

The particle sizes obtained from TEM for the final products with pristine or modified clays are consistent with the data obtained by light scattering measurement, i.e., the average particle size of latex with nanoclay is larger than latex without the clay. Figure 22-3b also illustrates that the nano-clay was detected as an irregular, transparent, and high aspect-ratio thin layer. When these very thin particles (1 nm

thickness) adsorb to latex particles by hydrophobic attraction force, particles are easily suspended to form a stable suspension even though they are not encapsulated by the polymer. Figure 22 - 2 illustrated that the final latex suspension made from the pristine clay is unstable, but the latex prepared by using the modified clay is very stable and no phase separation occurred after centrifugation with 10,000 rpm for 30 minutes.

The morphologies of the clay particles in the composites made from both unmodified and modified saponite particles were examined using TEM. To make a thin composite film for TEM observation, the final composite suspension was directly dropped on a TEM grid and allowed it to dry at room temperature. After that, the samples on the grids were heated up to 120 ^{o}C (above the glass transition temperature of polystyrene) to form a thin film. As shown in the Figure 23(a), when unmodified clay was used in the polymerization, the saponite particles aggregated together in the polymer matrix. However, if the saponite particles were pre-modified by long hydrophobic surfactant OTAB, the saponite particles were intercalated and uniformly dispersed in the polystyrene matrix. The morphology of the composite made from modified clay is shown in Figure 23(b).

5.4 Conclusions

Stable water-based polymer nanoclay colloids containing anisotropic saponite clay platelets have been synthesized by miniemulsion polymerization in this study. The polymer-nanoclay composite contains clay platelets with the intercalated structure, and the final latex suspension is stable up to 5 $wt.\%$ of clay in the polymer. Further increase of clay content in the monomer will result in the formation of monomer gel, which is difficult to be used for miniemulsion polymerization. The modification of saponite by cationic OTAB is critical not only for intercalation but also for a hydrophobic surface so that the clay particles can be easily dispersed in the monomer

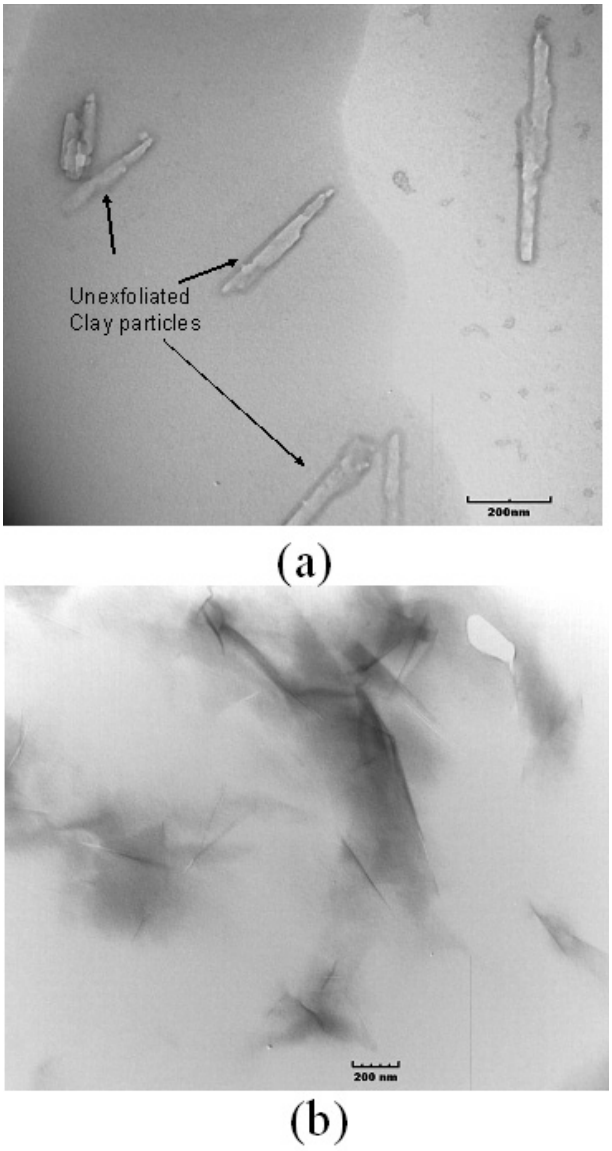


Figure 23: TEM images of the polystyrene nanosaponite composite film after melting: (a) unmodified saponite, (b) modified saponite in polystyrene matrix

phase during the miniemulsion polymerization. The presence of the costabilizer has a synergistic influence on the final latex stability. The result of polymerization kinetics indicates that the addition of nanoclay platelet reduces the polymerization rate. Finally, the TEM observation reveals that the surface modified organophilic clay is entrapped and firmly adheres onto the polystyrene latex particle surface. These entrapped nanoclay plates are stable in the suspension without precipitation for months. TEM observation of the final latex melting films illustrates that the surface modified organophilic clay is intercalated and uniformly distributed into polystyrene matrix after melting at the temperature higher than the Tg of polystyrene.

CHAPTER VI

POLYSTYRENE ENCAPSULATED NANOSAPONITE COMPOSITE LATEX VIA MINIMEULSION POLYMERIZATION AND THEIR MORPHOLOGIES

In our previous work, when montmorillonite with an average size about 450 nm (SEM estimation) was used, the encapsulation was unsuccessful because the plate size of montmorillonite is too big to be encapsulated by polymer latex particles. Instead of using montmorillonite, in last chapter, we reported that a stable composite suspension could be prepared by miniemulsion polymerization of styrene and saponite (200-300 nm plate size). Although the suspension prepared in that study was very stable, a large portion of saponite particles adhered only on the polymer latex surface rather than encapsulated inside the polymer latex. This chapter reports an improved approach to synthesize a stable water-based latex of polymer encapsulated nanoclay composite via miniemulsion polymerization based on the following two important strategies. First, instead of MMT (450 nm) and NSC (200 nm), the nanoclay used in this research is SSC with the average particle size of 50 nm, as shown in Figure 24, which has an average particle size of 50 nm and a uniform particle size distribution. Second, the nanoclay is surface-modified by a cationic surfactant VBTAC, which enables it to react with monomer styrene.[1]. The results in this chapter show

[1]This chapter has been modified from the following publication: Synthesis of polystyrene encapsulated nanosaponite composite latex via minimeulsion polymerization,Polymer, 2007, vol.48, n15, p4337-4343

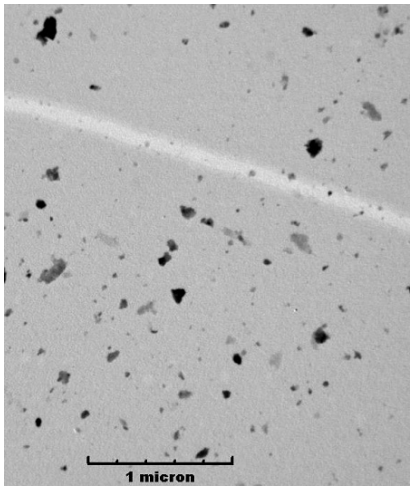


Figure 24: The TEM image of SSC clay dispersion in water

that VBTAC modified SSC could be fully exfoliated and encapsulated inside the polystyrene latex via in-situ miniemulsion polymerization. When the concentration of hexadecane (a costabilizer used in the miniemulsion polymerization) was high, final composite particles composed principally spherical particles with the size of less than 100 nm, and a small number of hemispherical or bowl-structured particles with a particle size from 100 to 1000 nm. The phase separation due to the existence of large amounts of hexadecane accounts for the formation of a variety of morphologies. The mechanism to form a variety of morphologies in the absence of as well as the presence of nanoclay is proposed.

6.1 Introduction

Polymer encapsulated inorganic particles with submicron scale have wide applications in cosmetics, pharmaceuticals, catalysis, optics, agriculture, coating and painting areas [60, 14, 15]. Miniemulsion polymerization is an in-situ method for preparing encapsulated particle suspensions. Tiark [105] and other authors studied the encapsulation of carbon black by miniemulsion polymerization. Erdem et al [32, 34, 35] prepared polystyrene encapsulated TiO_2 particles using miniemulsion polymerization

in the presence of hydrophilic TiO_2 particles. Landfester et al. [57, 89], encapsulated magnetite particles in polystyrene matrix using a miniemulsion polymerization process. K. Zhang et al. [122] synthesized a mono-dispersion silica-polymer core-shell microsphere via surface grafting and emulsion polymerization. S. Zhang et al. [123] synthesized SiO_2/polystyrene nanocomposite particles via miniemulsion polymerization by using methacryloxy (propyl) trimethoxysilane modified silica particles. Although the encapsulation of inorganic particles using miniemulsion polymerization technique has been extensively studied, most inorganic particles are spherical with a narrow size distribution. It is well known that nanoclay particles have a platy morphology with a broad size distribution, resulting in more difficulties in the dispersion and the encapsulation of these particles in monomer droplets and polymer latex in miniemulsion polymerization. Several researchers [117, 48, 46] have attempted to synthesize polymer encapsulated nanoclay composite via suspension, emulsion or miniemulsion polymerization method. Xu et al. [117] described a method to synthesize intercalated poly (styrene-co-methyl methacrylate)/clay nanocomposites through an emulsion polymerization by using a reactive surfactant, 2-acrylamide-2-methyl-1-propane sulfonic (AMPS). Huang and Brittain [48] synthesized the PMMA-layered silicate nanocomposites by suspension polymerization and emulsion polymerization. They simply mixed the unmodified clay into the aqueous phase or added the clay in post-polymerization step. The nanoclay particles were not encapsulated and the final suspension was not very stable. Herrera et al [46] synthesized the water-based polymer/clay nanocomposites by first chemically modifying the laponite clay minerals by silanting agents(-methyacryloxy propyl mono-, di, tri-methyl ethoxysilane) before the polymerization and then proceeding with seeded emulsion polymerization. However, the stability of the final latex was not reported.

It was found from our previous research that the particle size, the size distribution and the surface properties of nanoclay play synergistic roles on the encapsulation and

exfoliation degree as well as the final product stability in a miniemulsion polymerization process. For example, a high viscous solution or a gel of styrene were formed if the amount of the modified saponite in the monomer was higher than 4 $wt.\%$ because well dispersed nanoclay in the monomer significantly increased the oil phase viscosity, resulting in an unstable miniemulsion. For this reason, the stable composite suspension could not be prepared if the content of nanoclay is higher than 4 $wt.\%$.

In this chapter, we report a method to synthesize stable polystyrene nanoclay composite latex containing large amounts (up to 30 $wt.\%$) of fully-exfoliated and encapsulated nanoclay. The effect of clay amounts on the physical properties of final polymer nanoclay composite will be further studied. Contrary to our previous reports [96, 107] two important improvements are taken into account. Firstly, instead of the saponite NSC of 200-300 nm (measured by light scattering; Source Clay Repository of the Clay Mineral Society, University of Missouri) used in previous study, a saponite sample SSC with an average size of 50 nm (measured by light scattering; Kunimine industries Co., Ltd. Japan) was selected. Secondly, as an alternative of using long chain cationic surfactant such as OTAB for saponite modification, a short chain cationic surfactant with an unsaturated reactive group, VBTAC, was selected to pre-modify clay saponite. VBTAC can not only copolymerize with styrene, but also result in a low viscosity solution of nanoclay in the monomer phase.

6.2 Experiment

6.2.1 Materials

Na-saponite clay was supplied by Kunimine industries Co., Ltd. Japan. It was synthesized by a hydrothermal reaction with a ideal formula of

$$(Na_{0.49}Mg_{0.14})^{0.77+} - [(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03})O_{20}(OH)_4])^{0.77-}.$$

The cationic exchange capability of Na-saponite is 0.997 equivalent/kg. Its average particle size is approximately 50 nm (measured by light scattering) when it dispersed

in water. Other materials refer to the previous chapters.

6.2.2 Procedures

Surface modification of saponite clay by VBTAC: In a typical procedure, a suspension of 5 g of saponite in 400 ml of water was continuously stirred at room temperature for 2 hours until a transparent aqueous solution was obtained. Then, an aqueous solution of 1.2 g of VBTAC in 100 ml water was added to the solution. After continuous stirring of the suspension overnight at room temperature, a white precipitate was collected by centrifugation and washed with water and ethanol to remove the excess VBTAC until no chloride can be detected by silver nitrate. The sample was then dried in a vacuum oven at room temperature.

Miniemulsion polymerization of styrene in the presence of the modified saponite: In a typical run, as indicated by the recipe in Table 7, oil phase A composed of 1.2 g of co-stabilizer hexadecane and 0.24 g of AIBN, 12 g of the monomer styrene, and the varied amount of saponite (4-30 $wt.\%$ of the weight of monomer styrene), was subjected to magnetic stirring at room temperature for 30 minutes. The mixture was then exposed to ultrasonification for 4 minutes. Following that, oil phase A was poured into an aqueous phase B comprising of 1 g of TX-405 in 100 ml of water under vigorous mechanical stirring in an ice bath for 30 minutes. The miniemulsion composed of A and B was thus prepared by homogenization under ultrasonification for another 3 minutes and ready for subsequent polymerization.

The miniemulsion polymerization was carried out by degassing with N_2 at room temperature for 30 minutes first, and then increasing temperature to $80 \pm 2\,^{o}$C and keeping at this temperature for more than 6 hours under continuous mechanical stirring (600 rpm). The reaction was terminated by adding one drop of 2% 4-methoxyphenol solution into the miniemulsion .

6.2.3 Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Magna System 560 from Nicolet Company, with samples in pellet form from KBr. Thermogravimetric analysis (TGA) was performed using a Seiko TG/DTA 320 at a heating rate of $20\,^{o}\mathrm{C}/min$ under an air stream. X-ray powder diffraction patterns were recorded on a PW 1800 X-ray diffractometer (Philips, USA) using Cu, Ka ray ($\lambda = 1.54056^{0}A$) as the radiation source. A step size of 0.04^{o} and a scan step time of 0.5 s were adopted. The d (001) basal-spacing of the clay and the exfoliated clay were calculated using the Bragg equation:

The particle size and polydispersity were measured by a dynamic light scattering on a BI-200 SM Gohio-meter from Brookhaven Instrument Co. at a fixed angle of 90 degree, under laser ($\lambda = 632.8nm$) and with an aperture of 100 μm. The TEM observation was conducted on a JEOL 100C transmission electron microscope at an accelerating voltage of 100 KV and a beam current of 70 mA. The SEM analysis was carried out on a LEO 1530 thermally-assisted field emission (TFE) scanning electron microscope in combination with a thin window energy dispersive spectrometer (EDS) for microanalysis at an operating voltage of 3 KV and a working distance from 6 to 10 mm. The ultrasonification was conducted on a W-385 sonicator from the Heat System-Ultrasonics Inc., USA, at an output power level of 5 with a continuous mode, and a duty cycle of 70%. Centrifugation was conducted using Beckman 20 centrifuge at 10, 000 rpm for 30 minutes at room temperature.

6.3 Result and discussion

6.3.1 Modification and dispersion of nanosaponite

The pristine clay is hydrophilic and requires pre-modification to be dispersed in the monomer. It was found in our previous research, when long carbon-chain surfactant OTAB was used as a modifier, the saponite can change from hydrophilic to

Table 7: The Basic Recipe for the Miniemulsion Polymerization of Polystyrene (PS)/Clay Nanocomposite Latex Particles

Mixture	Ingredient	Amount (g)	Percentage in total ($wt.\%$)	percentage to monomer ($wt.\%$)
Oil Phase	styrene	12.0	10.4	100
	SSC	$0.48 - 3.6$	$0.4 - 3.0$	$4.0 - 30.0$
	Hexadecane	1.2	1.0	10.0
	AIBN	0.24	0.2	2.0
Water Phase	Tx-405	1.0	0.9	8.3
	Water	100.0	87.0	833.3

hydrophobic and well dispersed in organic phase. However, the viscosity of styrene monomer increased rapidly with the increase of the modified saponite content. As a consequence, stable miniemulsion could not be obtained if the saponite content is higher than 4 $wt.\%$ in the oil phase. In order to reduce the viscosity of the oil phase, in this research, a short carbon chain cationic surfactant VBTAC was selected as the modifier. This surfactant has an unsaturated group on one end that can react with the monomer styrene, and a cationic ammonium group that can absorb on the surface of hydrophilic clay to form organophilic clay. The experimental result shows that when VBTAC-modified saponite was dispersed in styrene monomer, the viscosity of the styrene phase was much lower than that OTAB modified saponite in styrene. Miniemulsion was stable up to 30 $wt.\%$ of VBTAC-modified nanoclay in the monomer phase. The composite latex obtained after polymerization was very stable and no remarkable precipitate was observed even after centrifugation at 10,000 rpm for 20 minutes. In addition, when a certain ratio ($> 30\%$) of VBTAC was replaced by OTAB, the viscosity of the monomer phase increased remarkably and the total nanoclay content in the monomer phase had to be reduced in order to obtain a stable miniemulsion.

The absorption amount of VBTAC on the clay saponite was measured by TGA.

It was shown that 78.6 $wt.\%$ of the total weight of VBTAC-modified saponite remained until temperature was up to 463.8 ^oC, which agrees well with the maximum cationic exchange capability of saponite (99.7 meq./100 g, 78.9 $wt.\%$ remained). This agreement means that the cationic ion exchange of saponite with VBTAC is complete.

The viscosity of the mixture of styrene with the organoclay modified by VBTAC is much lower than that modified by OTAB. FTIR spectrum, as shown in Figure 25, clearly demonstrated that both VBTAC and OTAB can enter the galleries and bond to saponite. The presence of the C-H stretching of OTAB at 3000-2840 cm^{-1} and the double bond C=C stretching $1667 - 1640 cm^{-1}$ of VBTAC, indicates the existence of OTAB or VBTAC in the pretreated saponite samples. The intercalation of the organo-saponite before and after polymerization was investigated using XRD. The dispersion of organoclay in styrene after 4-minute ultrasonification and the final latex obtained from miniemulsion were freeze-dried, and then the powder of samples was used for XRD measurement. As shown in Figure 26, the VBTAC-modified saponite powders dried from water and from styrene have the interlayer spaces of 1.47 nm and 1.48 nm respectively. Figure 26 also clearly shows that the peak of the saponite disappears after the polymerization, which suggests a full exfoliation structure of the saponite nanoparticles in the final composite suspension.

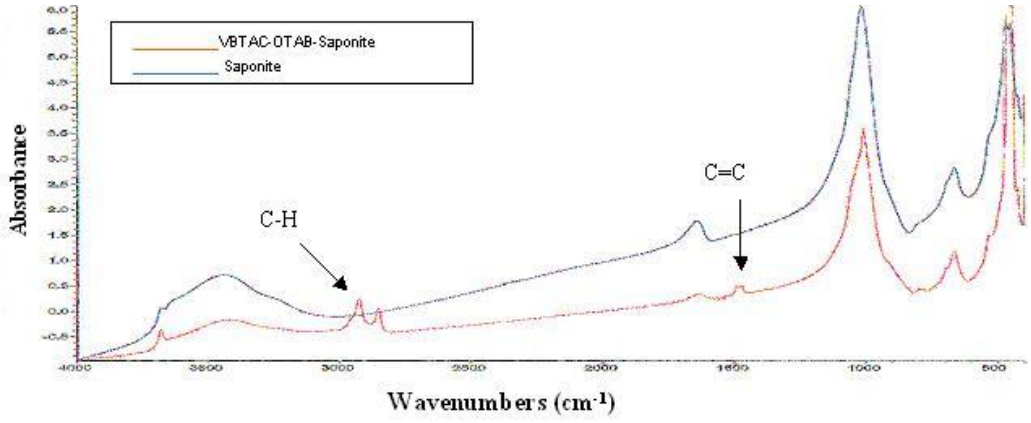


Figure 25: The FTIR spectra of the unmodified saponite and VBTAC/OTAB modified saponite with KBr pellets

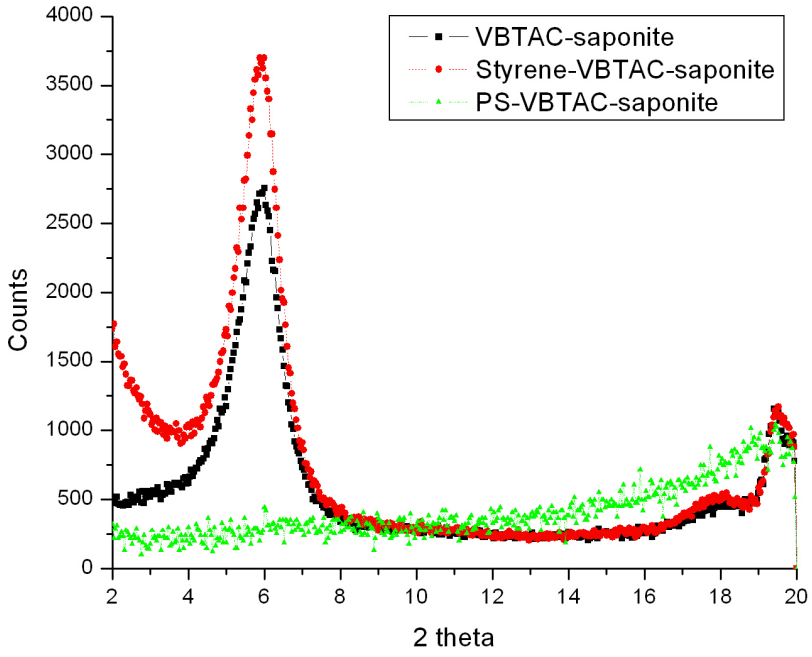


Figure 26: XRD spectra of VBTAC modified saponite, styrene dispersed VBTAC-saponite, and polystyrene exfoliated VBTAC-saponite

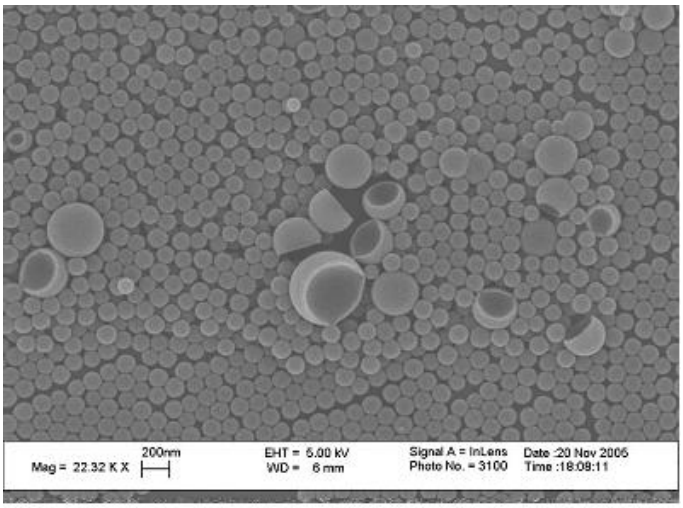
6.3.2 Morphology of polystyrene encapsulated organo-saponite composite latex

The SEM and TEM images shown in Figure 27 (a) and (b) indicate that particles with various morphologies are presented in the final product of the polystyrene-saponite composite suspension. The final composite mainly consists of spherical particles less than 100nm. However, some particles with the hemispherical or bowl morphologies with the particle sizes from approximately 100 nm to 1000 nm exist in the final product. The surfaces of both types of particles are smooth, and no clay particles can be observed. Furthermore, as shown in Table 8, the average particle size (measured by light scattering) of the final product in the presence of organoclay was larger and had a broader particle size distribution in comparison to that in the absence of organoclay.

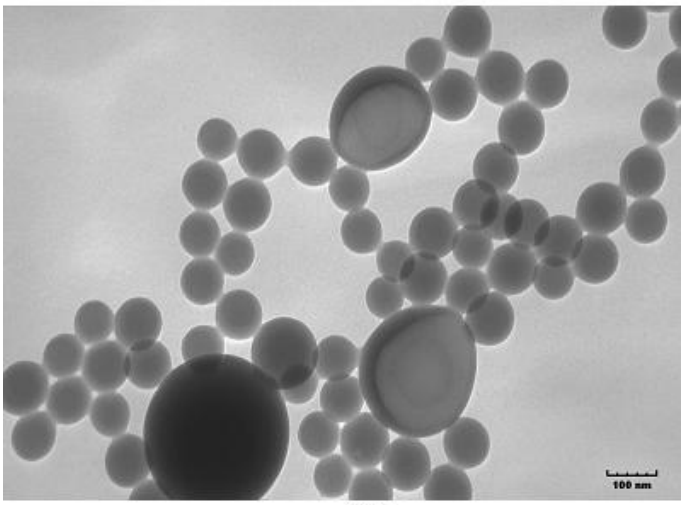
Table 8: The particle size and its distribution of polystyrene latex particles in the presence and absence of modified saponite measured by light scattering

	Average Diameter(nm)	PDI	Particle Size Distribution
PS latex without clay	161.4	0.117	Below 218.31nm: 96% Between 218.31nm and 2000nm: 4%
PS latex with 4$wt.$%clay	208.7	0.232	Below 232.40nm: 81% Between 232.40nm and 2000nm: 19%

In order to clarify the morphology of saponite particles inside the polymer latex, a dilute latex suspension was dropped on a TEM grid and dried at room temperature. The dried composite particles were then heated to high temperature (160 ^{o}C) to allow the polystyrene spreading on the TEM grid to form a thin film. TEM images of Figure 28 show the morphologies of the polystyrene organo-saponite composite latex (a) before and (b) after melting. The TEM pictures show that the particles are uniformly dispersed on TEM grid with no organo-saponite observed before melting. Thus, the organo-saponite particles must be encapsulated inside the final latex particles made by miniemulsion polymerization. Figure 29 shows the elemental composition of final polystyrene nanosaponite composite particles. This EDS spectrum provides further



(a)



(b)

Figure 27: SEM and TEM images of polystyrene nanosaponite composite latex particles via miniemulsion polymerization in the presence of 10% organosaponite based on the weight of the monomer styrene: (a) SEM, (b) TEM

evidence that the silicon is within the final latex particles although it could not be seen from the latex surface, suggesting the encapsulation of the saponite by polymer particles.

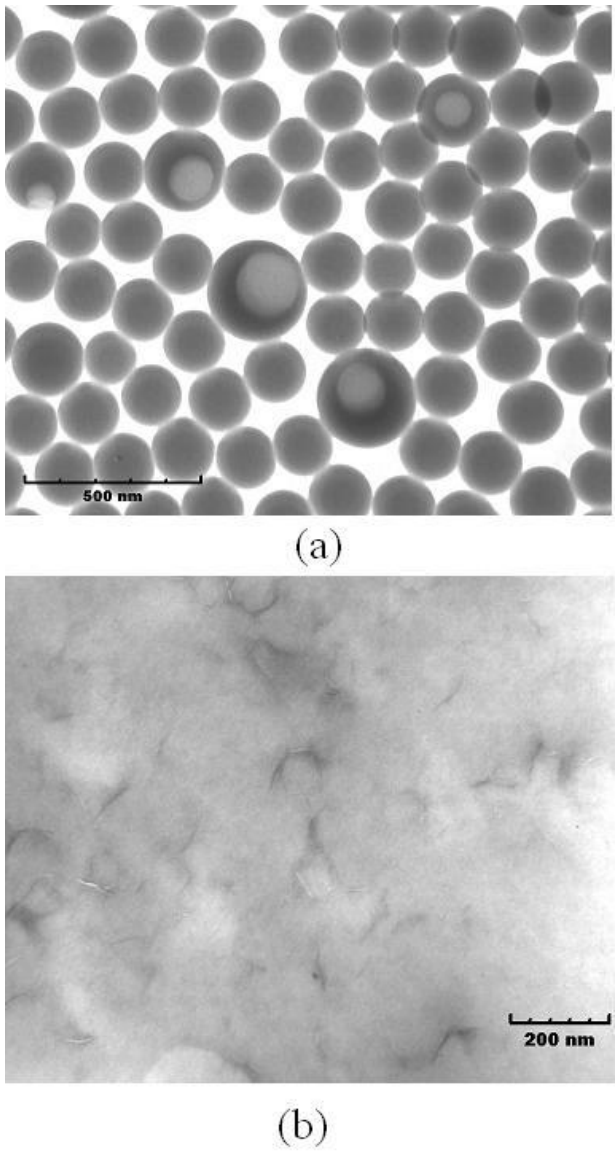


Figure 28: TEM images of the polystyrene organo-saponite composite latex: (a) before melting, (b) after melting

Figure 30 shows the polystyrene nanosaponite composite film after melting in the presence of the unmodified saponite (a) and the modified saponite (b). When the unmodified saponite was used, the platy saponite particles with an un-exfoliated

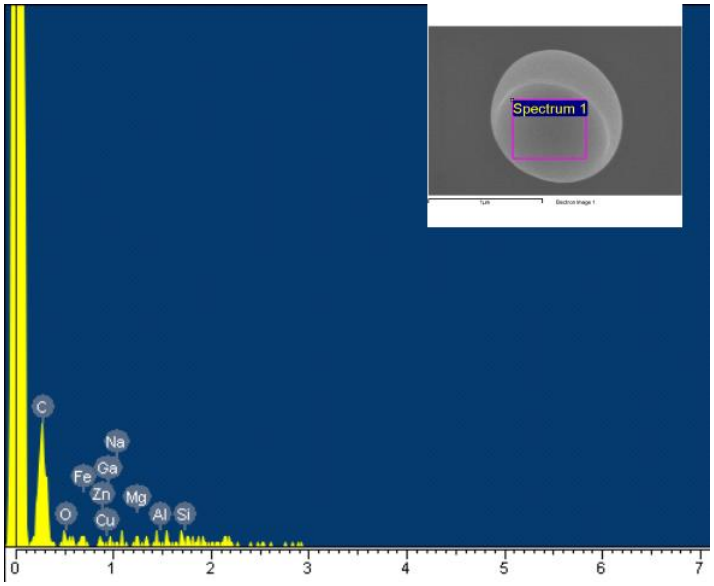


Figure 29: The EDS spectra of polystyrene nanosaponite composite latex particles

morphology were observed. However, exfoliated saponite nanolayers are uniformly dispersed in the polystyrene matrix of the polymer thin film made from VBTAC modified saponite. This result further proves that the organo-saponite particles are not only encapsulated but also exfoliated inside polystyrene latex particles.

6.3.3 Morphologies of final latex particles

As shown in Figure 27, the final polystyrene-saponite composite particles via miniemulsion polymerization using an oil-soluble initiator AIBN and non-ionic surfactant TX-405 are composed of two groups of particles: a spherical particle with a size less than 100 nm and hemispherical, or bowl, structured particle with a size from approximately 100 nm to 1000 nm. In order to understand the role of nanoclay in the formation of the hemispherical and bowl structured particles, more experiments were conducted in the absence of organoclay. The results indicate that pure polystyrene latex is composed of similar morphologies at the same polymerization conditions. It has been known that the initiation inside a droplet is the dominant reaction mechanism in a miniemulsion polymerization. It is also known that almost no new particles are

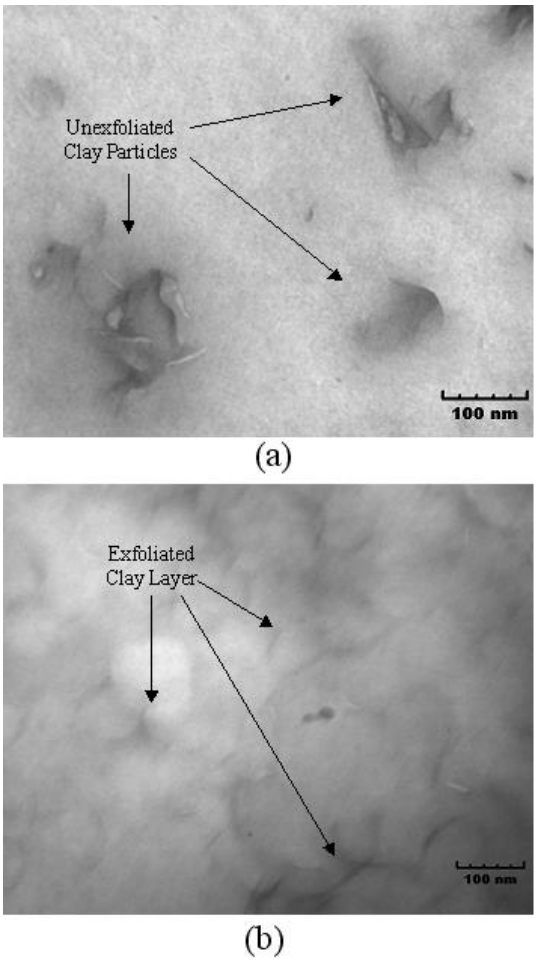


Figure 30: TEM images of the polystyrene nanosaponite composite film after melting. Unmodified saponite (a) and modified saponite (b) in polystyrene matrix

produced during polymerization if $1-2\%$ costabilizer is used in a miniemulsion polymerization because costabilizer can effectively suppress the coalescence of droplets and retard Oswald ripening [58]. Therefore, the traditional miniemulsion mechanism does not make a reasonable explanation for the formation of the particles with the varied morphologies.

Figure 31 shows the SEM images of the final latex particles prepared in the absence of hexadecane (co-stabilizer in miniemulsion polymerization) and saponite. It can be seen that the spherical latex particles are uniform with a diameter less than 100 nm. Compared to the SEM image of the latex prepared with 10% of hexadecane (Figure 27), it can be concluded that costabilizer hexadecane plays an important role in the formation of various morphologies such as large hemispheres or bowls. Furthermore, the experiment in the absence of hexadecane but with nanosaponite indicates that the final latex particles have the same size and size distribution as SEM image in Figure 31. It excluded the possibility of the nanoclay is the main factor for affecting the particle size and size distribution. Landfester et al. [104] reported similar morphologies when large amounts of costabilizer hexadecane ($> 10\%$) were used in miniemulsion polymerization. Because polystyrene is insoluble in hexadecane, the phase separation of polystyrene and hexadecane inside the miniemulsion droplets occurred if hexadecane concentration in the latex is high. It is believed that the hexadecane was removed by high vacuum in SEM sample preparation, resulting in polystyrene hemispheres or bowls. The emulsion coalition during polymerization was believed to account for the formation of some large particles in the final products.

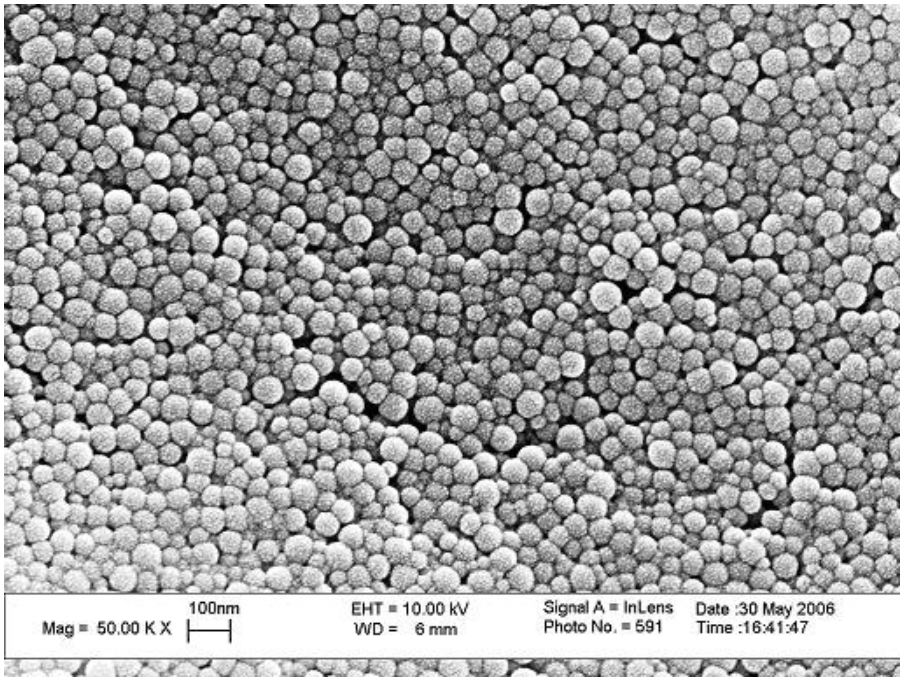


Figure 31: SEM images of polystyrene latex in the absence of hexadecane

6.4 The mechanism to form a variety of morphologies of polystyrene/SSC composite latex particles via miniemulsion polymerization

The polystyrene/clay composite latex particles synthesized by miniemulsion polymerization are constructed by two groups of particles. The principal particles are spherical particles with the size of less than 100 nm and a core shell structure. A small number of particles are hemishperical and bowl-structural particles with a particle size from approximately 100 to 1000 nm. The phase separation due to the existence of large amounts of hexadecane contributes to the formation of this variety of morphologies. In this section, we attempt to clarify the mechanism to form this variety of morphologies of polystyrene/clay composite latex particles based on the information gathered from more supporting experiments. As we know, the asymmetric nanoparticles are significant for the preparation of self-assembly building blocks, which have numerous potential applications. This section may provide a possible method to produce the

asymmetric nanoparticles for future research.

The control of particle morphologies of polymer is essential for application in coating, adhesives [98], drug delivery, medical diagnostics [101] and semiconductor manufacturing [55]. Currently, there is an increased interest in synthesis of particles or microbeads with non-spherical or asymmetrical spherical shapes [85]. Particles with an asymmetric shape could be used as anisotropic building blocks for advanced material construction. Physical methods such as capillary liquid break-up [76], microfabrication [72], and uniaxial stretching of spherical polymer beads [66] are developed to prepare asymmetrical particles. However, these methods are complex because they require unique technology and special substrates and facilities. Furthermore, the particle size is usually in micrometer-scale but not in nanometer-scale. Chemical methods for synthesizing unsymmetrical particles with different morphologies, such as core shell [123], hemispherical [82], and bowl shape [63] are usually prepared via a seeded dispersion or emulsion polymerization approach. Du et. al [31, 30] and others [43, 2] prepared micron and submicron-sized polymer particles with different morphologies by seeded dispersion or emulsion polymerization. The produced latexes exhibited a wide variety of particle morphologies such as core-shell, hemispherical, or inverted core-shell structures. The mechanism for producing various morphologies is based on the heterogeneous structures generated by the phase separation of different polymers in the particles after polymerization. Final particles usually contain two or more immiscible particles, therefore, the morphology of particles is not a true hemisphere.

The phase separation method was also applied to the formation of hollow particles and microcapsules of hydrophobic polymers[95]. In general, the monomer is chosen to be soluble in the core phase while the forming polymer is not. Then the forming polymer phase separates from the core and deposits itself at the oil-water interface to form microcapsules [65, 71] with the aid of the following solvent extraction or evaporation.

As aforementioned Tiarks et al. [105] work, polymeric nanocapsules were prepared by a miniemulsion polymerization method in the presence of a large amount of a hydrophobe. The structure of final latex particles could be adjusted from the whole core-shell to particle engulfed structure of independent particles. The morphologies were determined by the type of surfactant chosen, the polarity of the monomer, and the choice of the hydrophobe which modified either the polymer/hydrophobe or water/polymer interface and determined the degree of engulfing. However, our system is more complex than Tiarks' miniemulsion system because of the inclusion of nanoclay. How nanoclay impacts the morphologies of final polymer nanoclay composite latex needs to be clarified. The publications for the asymmetric structures of polymer nanoclay composite particles are quite limited. For example, Bourgeat-lami [15] conducted a series of research to synthesize polymer/laponite composite colloids through seeded emulsion polymerization and another "miniemulsion-like" polymerization. They reveal that the suspensions were made of stacky agglomerates containing three to four individual platelets. The polymer latex grew on one side of laponite, but not on both side of laponite. Furthermore, Their results also show that the larger the laponite particle size, the larger the size and the size distribution of the composite particles. In this section, we attempt to propose the mechanism for the formation of the polymer/SSC composite latex particles with a variety of morphologies in consideration of the coherent effects of nanoclay particles as a template and phase separation.

6.4.1 The formation of hemispherical polystyrene/nanoclay composite particles via a single-step miniemulsion polymerization using Nanosaponite particles as a template

A general synthesis procedure is described in the experimental part of this section. The hemispheric polystyrene/saponite composite latex particles were found by first pre-modification of pristine saponite clay with the cationic monomer (ar-vinylbenzyl)

trimethylammonium chloride (VBTAC) and/or a cationic surfactant, and followed subsequently by a miniemulsion polymerization of the modified clay with styrene. Figure 32 a and b shows that the morphologies of the polystyrene nano-saponite composite latex particles with an addition of 4.0% of the modified organophilic saponite clay. Two groups of particles were observed. One group of the particles consists of spherical particles less than 100 nm, which is believed to be pure polystyrene particles and polystyrene encapsulated small size of nanosaponite, which was discussed in detail in the first part of this section. The other group of particles consists of truncated or hemispherical particles with a size range from approximately 100 to 1000 nm, usually less than one micron. It is observed that there is a thin layer of the platelet saponite clay on the truncated plane, as indicated by Figure 32 b. It is believed that this saponite thin layer acts as a template during the miniemulsion polymerization, and the size and the shape of the composite hemispheric latex particles are determined by this saponite template, which will be further discussed in the later part of this section. As indicated in the arrowed area of Figure 32 b, it is clearly observed that the clay plates are attached to the planar surface of the hemispherical particles as a template.

In order to track the shape evolution of the hemispherical particle formation during the reaction process, the samples were taken out from the reactor at different times during the polymerization, and then the morphologies were observed by transmission electron microscopy (TEM) analysis. It was observed from Figure 33 a that only saponite plates were observed after 15-minute polymerization. However, after 30-minute reaction, the polystyrene particles that attached at one or both sides of the planar clay saponite were observed (b). The TEM images of the latex after 45- and 90-minute reactions (Figure 33 c and d) indicated the formation of spherical polystyrene particles (possibly some core–shell particles too), hemispherical and truncated spherical particles.

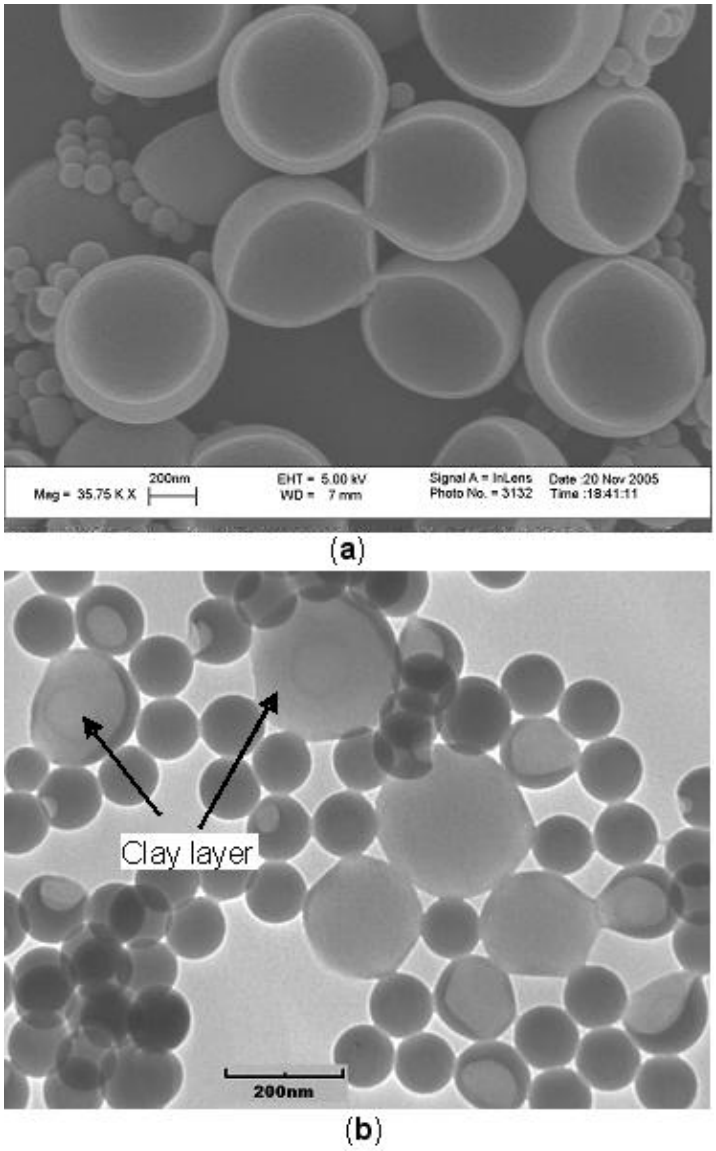


Figure 32: The polystyrene SSC latex particles with 4% VBTAC modified saponite. (a) SEM and (b) TEM

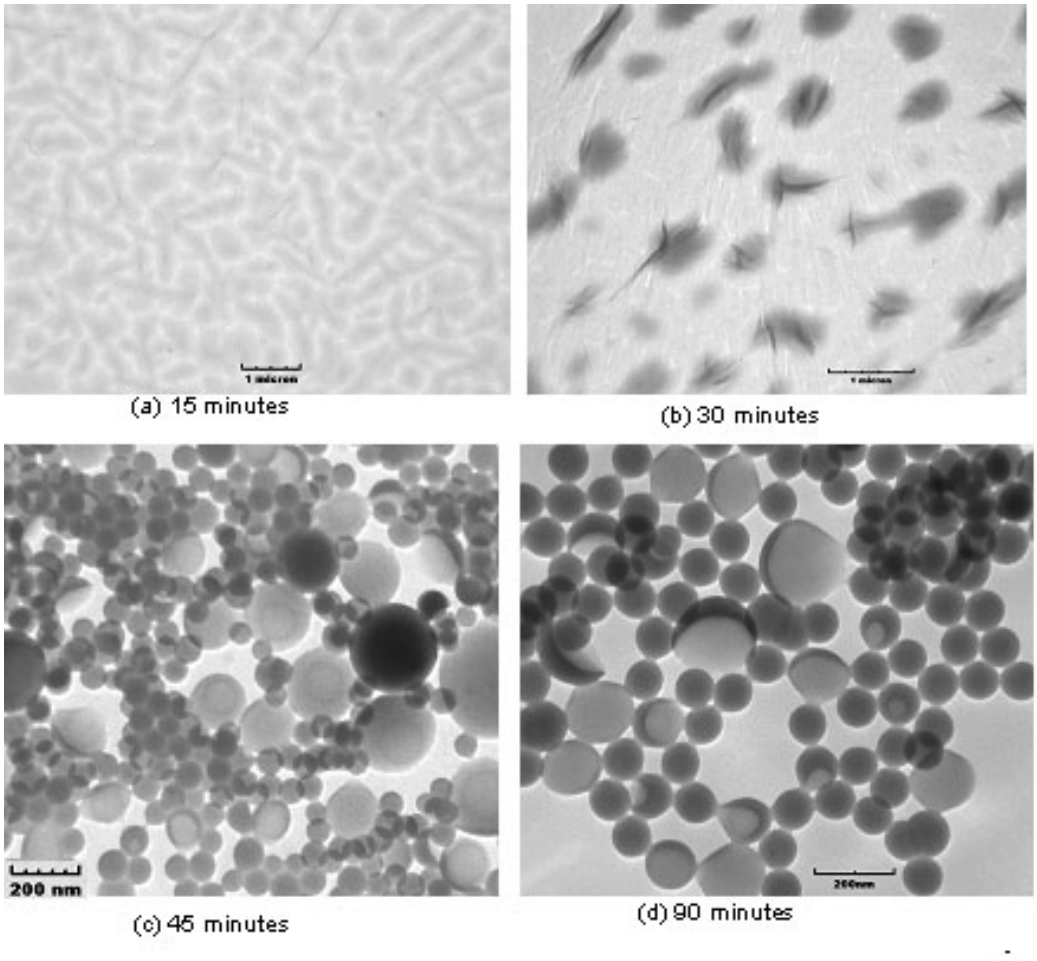


Figure 33: TEM show the morphologies of polystyrene/VBTAC-saponite composite latex particles at different times during polymerization

6.4.2 The mechanisms for the formation of hemispherical particles in the absence and the presence of nanosaponite

Figure 34 and 35 show the SEM images of polystyrene latex particles in the presence of 10% of hexadecane and in the presence and the absence of nanosaponite, respectively. As shown in Figure 34, in the absence of nanoclay, the pure polystyrene latex particles principally consist of the spherical particles with the particle size of $\leq 100nm$. However, there are a number of hollow particles with a bowl or hemispherical structure in final particles. The particle size (approximately 200 nm to 1 μm) of these assymetric particles is greater than that of uniform spherical particles and their particle size distribution is broader than that of spherical particles as well. As illustrated in Figure 35 and the aforementioned figures, in the presence of nanosaponite, a number of hemispherical or bowl structural particles exist in the system as well. On the contrary, no hollow structural particles appear in comparison with that in the absence of nanoclay. Instead, the saponite platenet was observed to attach on the surface of these particles with a hemispherical or bowl structure. The results indicate that the morphology difference in the presence of nanoclay from the absence of nanoclay should be attributed to different mechanisms.

Figure 36 shows the scheme of the possible mechanism for the formation of polystyrene latex particles with a hemispherical or bowl structure in the absence of nanoclay. In polystyrene miniemulsion polymerizaton using AIBN as the initiator, two types of nucleation mechanisms, particle nucleation and homogeneous nucleation, coexisted. Both the initiator AIBN slightly dissolved in the aqueous phase and the monomer diffused from the oil droplet to the aqueous phase induced homogeneous nucleation, which breaks the 1:1 copy of ideal miniemulsion polymerization and leads to the formation of large particles during polymerization. Furthermore, the emulsion collision during agitation produced a larger particle size of emulsion droplets as well. A broad range of particle size distribution was reported in the literature reviewed

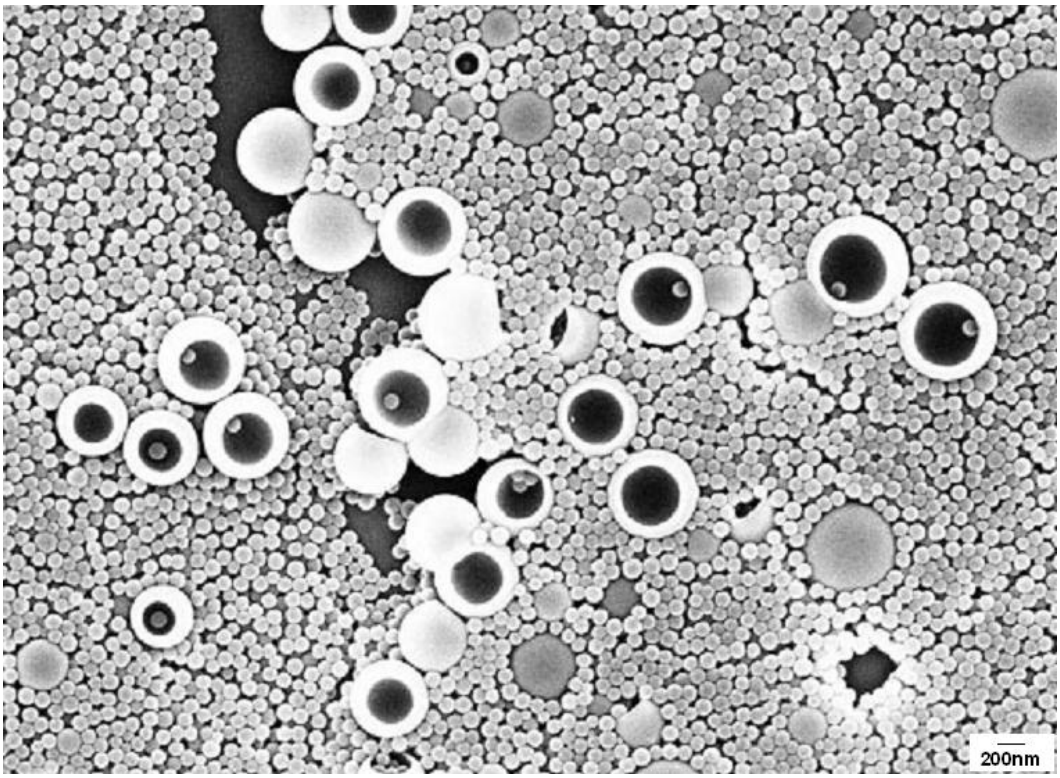


Figure 34: Polystyrene latex prepared by miniemulsion polymerization without clay and with 10% hexadecane

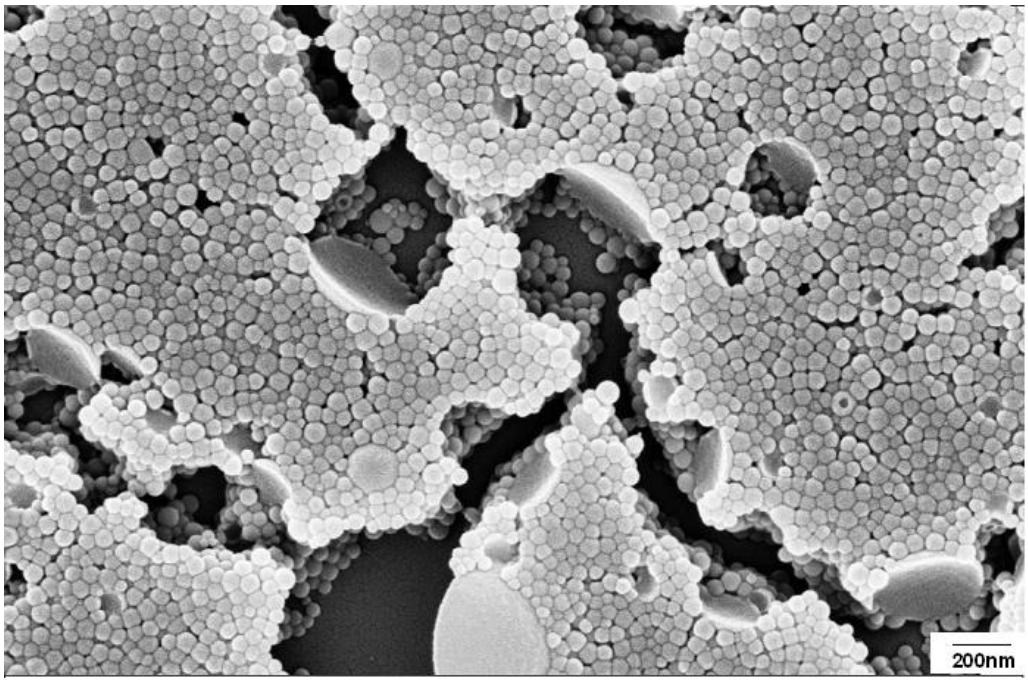


Figure 35: Polystyrene latex prepared by miniemulsion polymerization in the presence of 4% modified clay latex and 10% hexadecane

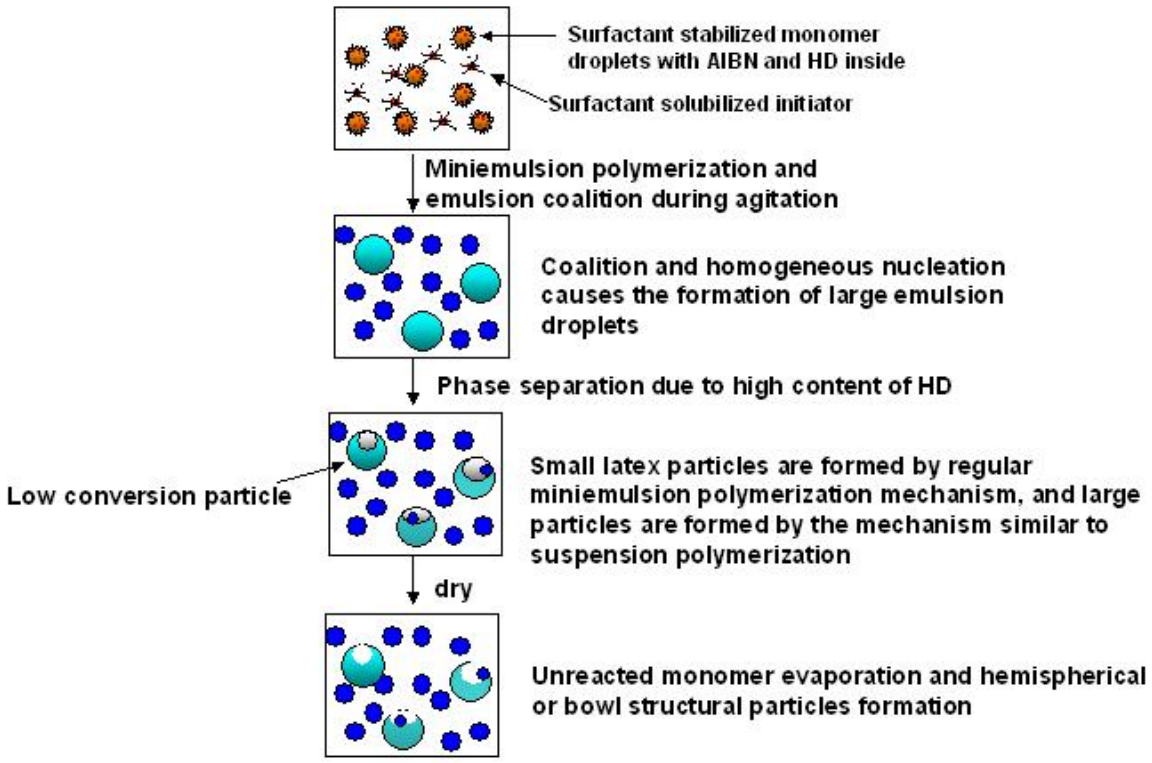


Figure 36: The scheme of the possible mechanism for the formation of hollow hemispherical polystyrene particles in the presence of 10%hexadecane via miniemulsion polymerization

in chapter II. The principle spherical particles with the size less that 100 nm were formed by following regular miniemulsion polymerization mechanism. A small number of large particles with polymer, HD and unreacted monomer was also produced by following a mechanism similar to suspension polymerization. Phase separation occurred and polymer migrated to the water/droplet interface during vacuum drying the SEM sample. Meanwhile the unreacted monomer evaporated from final latex particles during vacuum drying, therefore, the hemispherical or bowl structural particles with a hollow-like structure were obtained.

Figure 37 illustrates the scheme of the polystyrene/clay nanocomposite formation during the miniemulsion polymerization process. As the first step, the cationic monomer, hexadecane (co-stabilizer), and hydrophobically modified saponite clay were homogeneously dispersed in styrene monomer phase with the aid of ultrasonification to form intercalated nanoclay particles. The oil phase was then mixed with an aqueous phase containing surfactant TX-405 under vigorous mechanical stirring to form a miniemulsion. Because the clay surface was modified to less hydrophilic by the cationic monomer VBTAC, the monomer drop can either fully spread or remain as an individual droplet on the clay surface with a certain contact angle. In our system, the average size of the styrene miniemulsion droplet is about 90 nm, and most saponite particles are in the range of a few hundred nanometers. Clearly, most clay particles are too big to be engulfed by the small monomer droplets. The large clay plates may function as a template for the monomer droplet to form a hemisphere morphology instead. However, if the clay plate size is too big, the particles are usually unstable during the polymerization, resulting in the formation of clay-polymer aggregates. This is really the case in this system in that a small amount of clay-polymer composite precipitate was always detected after the polymerization, and large clay particles were usually observed as in precipitates form. It should be noted that not only the particle size, but also the spreading ability of monomer on the clay surface together

determine the droplet morphology. For a typical emulsion polymerization system comprised mainly of an oily monomer, clay, and water, the spreading coefficient, S, of the oil can be expressed as follows:

$$S = S_{clay-oil} - (S_{oil-water} + S_{oil-clay}) \tag{16}$$

Where S_{ij} denotes for the interfacial tension between the components as indicated in the subscription. In this study, because the pre-modification of the saponite clay with VBTAC can significantly reduce the $S_{oil-clay}$ and increase the $S_{clay-water}$, the morphology of the oil drop on the clay surface can thus be changed from non-wetting to fully spreading, as delineated in the plot. When the S value and the particle size of the nanoclay template matched at a suitable value, the hemispheric particles could be formed, as shown in the shaded area in Figure 37. It should be noted that although premodification using OTAB alone may also achieve desirable contact angle of the monomer on the clay surface, no hemispherical nanocomposite particles, however, were obtained if without the VBTAC in the premodification process. A possible explanation for this is that the polymer particles formed on the surface of the clay template can be easily peeled off under mechanical shearing force if there was no covalent bonding between the polymer and the clay template. When the VBTAC was used, however, the VBTAC molecules not only reduced the hydrophilicity of the clay particles but also formed anchoring site to govern the growth and propagating of the macromolecular chain on the clay surface.

6.5 Conclusion

This chapter presents a one-step method to synthesize polystyrene encapsulated nanoclay composite latex via miniemulsion polymerization. The particle size of nanoclay and its pre-modification are two important factors for preparing stable miniemulsion before polymerization and latex after polymerization. The correct pretreatment

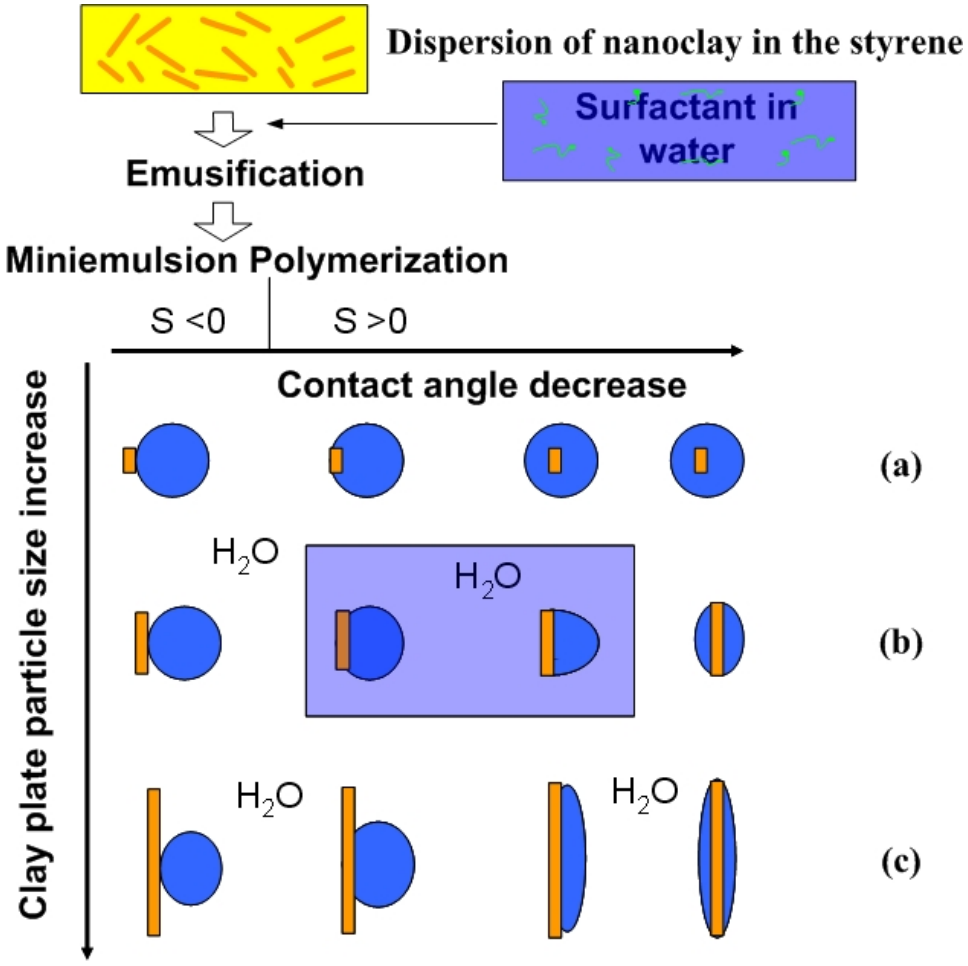


Figure 37: The relationship among the spreading properties, clay plate size and the morphology of final particles. (a) The particle is too small, it is engulfed in the polymer latex if $S > 0$; (b) The central block represents the suitable condition for hemisphere formation; (c) The particle is too big, it precipitates during polymerization.

chemistry is also one of the critical factors for encapsulation and exfoliation of nanoclay inside the latex particles. For the saponite with the average particle size of 50 nm and pre-modified by a monomer reactive cationic surfactant VBTAC, polystyrene latexes containing large amounts (up to 30%) of organo-saponite were obtained. The final polystyrene nanoclay composite particles were composed of two groups of particles, the majority of which were spherical particles less than 100 nm, and the minority of which were hemispherical or bowl particles from 100 nm to 1000 nm. Furthermore, the morphologies of final latex particles in the presence of the unmodified and the modified nanoclay and its melting film above 160 ^{o}C were investigated. The results further proved that VBTAC- modified nanoclay was exfoliated and encapsulated inside the polymer latex particles, while the unmodified nanoclay platelet was not exfoliated.

Furthermore, the mechanism to form a variety of morphologies and a broad size distribution for final polystyrene latex particles was investigated. In the absence of nanoclay, except the principle spherical solid particles, the hollow particles with hemispherical or bowl structures were formed in final polystyrene latex particles. The mechanism to form hollow particles with a hemispherical or bowl structure, attributes to the phase separation in the presence of large amounts of hydrophobe hexadecane. In the presence of nanoclay, the polystyrene/nanosaponite composite particles primarily consisted of spherical particles with a core-shell structure and the particle size less than 100 nm. However, a number of spherical or truncated (crescent) particles also existed in the system. Both phase separation and the inclusion of nanoclay contribute to the formation of hemispherical or truncated (crescent) particles. The intercalated nanoclay with a proper particle size could function as a template to form polymer/clay composite particles with a unsymmetrical morphology. Both the particle size and the surface hydrophobicity of the clay are important in determining the final particle shape.

CHAPTER VII

KINETICS OF MINIEMUSLION POLYMERIZATION OF STYRENE IN THE PRESENCE OF ORGANOCLAY

In chapter VI, a stable water-based suspension of polymer encapsulated nanoclay NSC composite could be synthesized using VBTAC modified clay NSC. We also found that the rate of polymerization and the fractional conversion decreased with the amount of nanoclay based on the study of chapter V. In this chapter, we further examine the impact of nanoclay on the miniemulsion polymerization kinetics of styrene, and the reason why the nanoclay deteriorates the rate of polymerization and the fractional conversion. The hindrance of nanoclay on the polymerization rate and the fractional conversion is mainly caused by the destabilization of the miniemulison in the presence of organoclay particles. The increase in the monomer viscosity and the decrease in the diffusion rate of the monomer and the living polymer inside the monomer droplet also accounts for the reduction in the polymerization rate. The results also show that in the presence of nanoclay, the molecular weight of polystyrene nanoclay composites is lower and the polydispersibility of the particle size of final composite latex is greater than that of pure styrene miniemulsion polymerization.[1]

[1]This chapter has been modified from the paper submitted to *Journal of polymer science*: kinetics of miniemulsion polymerization of styrene in the presence of organoclay

7.1 Introduction

Although there are numerous publications focusing on miniemulsion polymerization in the presence of different inorganic particles, the effect of inorganic particles on the kinetics and nucleation mechanism of miniemulsion polymerization has been seldom investigated. In aspects of polymerization kinetics in the presence of inorganic particles, few researcher reports the effect of inorganic solid on the conversion and the miniemulsion polymerization rate under the specified miniemulsion polymerization conditions. There are several publications addressing that the inorganic particles do not influence the conversion and the rate of polymerization in the miniemulsion polymerization [88, 13, 73, 61] but others reports that the addition of inorganic particles, such as SiO_2, TiO_2, $CaCO_3$ and Ag, may reduce both the conversion and the reaction rate during an emulsion or a suspension polymerization process [75, 119]. We have previously found that the presence of nanoclay reduced both the rate of polymerization and the final conversion of styrene miniemulsion polymerization when OTAB modified NSC was added to the reaction system [107]. Although both positive and negative effects of fine solid particles on the miniemulsion polymerization conversion and rate were observed, there has been no symmetrically study about the mechanism of why these can be affected by the fine solid particles. In this paper, the kinetics and the conversion of styrene miniemulsion polymerization in the presence of organoclay is studied in detail.

The droplet nucleation (monomer phase initiation) has been reported as the dominant nucleation mechanism for miniemulsion polymerization [7], and the homogeneous nucleation (water phase initiation) has been addressed to act as a minor nucleation mechanism as well [25, 90, 23]. The particle number per unit aqueous phase before and after polymerization provides important information about the nucleation mechanism of miniemulsion polymerization. Generally speaking, the particle number per unit aqueous phase after polymerization increases if both droplet nucleation and

homogeneous nucleation exist simultaneously.

Both the miniemulsion kinetics and nucleation mechanism are related to its stability, especially in the presence of the clay. To create a stable miniemulsion, the droplets must be stabilized against molecular diffusion degradation (Ostwald ripening or $\tau 1$ mechanism) as well as against coalescence by collisions ($\tau 2$ mechanism). It is well known that costabilizers such as hexadecane and high molecular weight alcohol act as osmotic agents to block monomer ripening. However, droplet coalescence plays an important role in destabilizing monomer miniemulsion. The instability of the miniemulsion affects the number of monomer droplets and therefore the rate of polymerization, the particle size and the molecular weight of the final product. The formation of small droplets is a requirement for the enhancement in both droplet nucleation and the polymerization rate. In an ideal miniemulsion polymerization with 1:1 copy of droplets, the smaller the monomer particle is, the smaller the particle size of the final product. However, practically it is difficult to obtain 1:1 copy during miniemulsion polymerization. Landfester and coworkers demonstrate that the polymer particle stability, rather than monomer ripening, plays an important role in determining final droplet size in miniemulsion polymerization . In respect of the molecular weight of the polymer via miniemulsion polymerization [4], Lou et al. [67] reports that the instability of miniemulsion has an influence on the molecular weight distribution of the final product.

7.2 Experiment

7.2.1 Materials

Materials refers to chapter VI.

7.2.2 Procedures

Surface modification of the clay SSC by VBTAC or OTAB and miniemulsion polymerization of styrene in the presence of organoclay(VBTAC-SSC) refers to the same

procedures in chapter V and VI.

Preparation of styrene miniemulsion with the different sizes of nanoclay: Three types of nanoclays with different average particle sizes were used in this study. The included particles were SSC with an average particle size of 50 nm, NSC with an average particle size of 200 nm, and MMT with an average particle size of 450 nm. All types of nanoclays were pre-modified by OTAB with the aforementioned surface modification method. After that, the styrene nanoclay miniemulsions were prepared in the absence of initiator AIBN following the same procedure for the preparation of the miniemulsions before polymerization. In this set of tests, only a relative low level of organoclay (from 0.05 to $1wt.\%$ of the weight of monomer styrene) was added into miniemulsions. The prepared miniemulsions were used for further particle size measurement.

The conversion measurements: The conversion was determined using gravimetric method. Miniemulsion samples (approximately 10 g) were taken from the reactor at different reaction time from 0 to 120 minutes followed by adding a drop of inhibitor. The samples were then placed on aluminum pans inside the fume hood overnight to remove the monomer styrene by evaporation. Thereafter the samples were vacuum-dried in an oven at $80\,^oC$ to a constant weight. The amounts of the clay in the polymer particles were determined by a gravimetric method after the polymer was burned out at $725\,^oC$ for 4 hours. The polymer concentration for each sample at time t was calculated by deducting the non-polymer concentration from the total monomer concentration. The conversion was determined by

$$Conversion = \frac{[M]_0 - [M]_t}{[M]_0} \tag{17}$$

Where $[M]_0$ and $[M]_t$ are the monomer concentrations at time 0 and t respectively.

7.2.3 Characterization

The particle size and the polydispersity of monomer droplets (or latex particles) were measured by a dynamic light scattering on a Malvern zetasizer 3000 from Malvern Co. at a fixed angle of 90 degree. The sample was diluted with 1% of Titron-405 water solution to adjust the concentration before the light scattering measurement. The reported monomer droplet size and latex particle size in this study represent an average of 10 runs and the error has been estimated to be 5% or less. Molecular weights were determined by gel permeation chromatography (GPC) by passing two columns. The front (Phenomenex) one has a pore size of 103 Angstroms, while the back (Viscotek) one is a mixed-bed column designed to give a linear calibration. A Waters 410 differential refractometer and Viscotek T60A detector provide data to the TriSEC 3.0 software (Viscotek). Chloroform was used both as eluent and as solvent for the samples. Solutions were made up to the overall concentrations of 3-8 mg polymer/ml liquid. The solutions were then filtered to remove any insoluble material and injected into the system, passing through a second filter before entering the columns and the detector. Poly (methylmethacrylate) standards were used for the calibration, with the molecular weights of these being corrected for the polymers formed in this work.

The ultrasonification was conducted on a W-385 sonicator from the Heat System-Ultrasonics Inc., USA, at an output power level of 4 or 5 with a continuous mode, and a duty cycle of 70%.

7.2.4 Calculations

The polymerization rate R_p is determined by conversion versus time curve, in which $R_p = [M]_0 dX/dt$ is the initial monomer concentration in aqueous phase (g/dm^3), X is fractional conversion and t is reaction time. dX/dt was determined by differentiating the fitting polynomial trendline of the X vs. t curve. The number of monomer droplets

or polymer latex particles per liter of aqueous phase ($N_{m,i}$ and $N_{p,f}$, particles/dm^3 H_2O) can be calculated from the droplet size of monomer and the particle size of polymer latex obtained by dynamic light scattering as described by

$$N = 6 \times [M]_0 X_f / \pi \rho D^3 \tag{18}$$

Where X_f is the final conversion or 1 (100% for monomer at the beginning of reaction), ρ is polymer (monomer) density (g/dm^3)and D is the average diameter (cm) of polymer latex (monomer) particles.

The average number of radicals per particle at maximum R_p can be calculated by [11]

$$\bar{n} = R_p N_A / K_p [M]_p N_p \tag{19}$$

Where, the monomer concentration in the particle $[M]_p$ can be expressed as [11]

$$[M]_p = \frac{1 - X_{Rp}/[M]_0}{1 - X_{Rp}/\rho_m + X_{Rp}/\rho_p} \tag{20}$$

Here X_{Rp} is the conversion at maximum R_p . ρ_m is the density of monomer (1.05 g/cm^3) and ρ_p is the density of the corresponding polymer (0.909 g/cm^3). is the propagation rate constant (490 $cm^3 \bullet mol^{-1} \bullet s^{-1}$) [16], $[M]_p$ is the monomer concentration in polymer particles ($10^4 g/mol$). N_p is estimated by the number of monomer particles per unit aqueous phase ($N_{m,i}$) because the choosing point (at maximum R_p) is close to the beginning of the reaction.

7.3 Result and Discussion

7.3.1 Styrene miniemulsion kinetics in the absence and the presence of different clay contents

SSC was used in the entire kinetics studies of hybrid styrene miniemulsions except where it is noted. The nanoclay concentration was varied from 0 $wt.\%$ to 12 $wt.\%$ (based on the weight of the monomer styrene). The influences of clay addition on the polymerization rate and the conversion are shown in Figure 38. The final conversion

(X_f) of styrene decreased when the saponite clay content was increased, as shown in Figures 38 and Table 9. The maximum conversion in the absence of clay reached approximately 94%, but it was dropped to 92%, 74%, and 72% when the clay content increased to 4%, 8%, and 12%, respectively. Figure 38 also shows that the conversion of the pure styrene system reached the maximum value at the reaction time of approximately 60 minutes and thereafter leveled off. The reaction time at the maximum conversion delayed to 80 minute, 90 minute, and 90 minute when 4%, 8%, and 12% nanoclay were added respectively. The reaction rate (R_p), as can be seen in Figure 39 and 40, indicates that in the beginning of a reaction (0-6min), the reaction rate dramatically increases for all systems. After the reaction rate had reached the maximum value, the rate of polymerization decreased for all systems. The dependence of the polymerization rate on polymerization time, as shown in Figure 39, follows the typical miniemulsion polymerization kinetics very well. It is however different from a classical emulsion polymerization where the maximum polymerization rate remains constant until the gelation state [11, 39].

Table 9: Parameters of styrene miniemulsion polymerization in the presence of different contents of SSC

Clay content(%)	0	4	8	12
$D_{m,i}(nm)$	208.7	227.1	371	762
$D_{p,f}(nm)$	161.4	208.7	291.9	480.7
$PDI_{m,i}$	0.379	0.743	1.000	1.000
$PDI_{p,f}$	0.117	0.232	0.250	0.280
$N_{m,i}(10^{17}/dm^3H_2O)$	0.232	0.180	0.042	0.005
$N_{p,f}(10^{17}/dm^3H_2O)$	0.408	0.185	0.058	0.012
$N_{p,f}/N_{m,i}$	1.759	1.026	1.386	2.483
$R_p(10^{-4}mol/dm^3H_2O/sec)$	3.81	2.38	1.75	1.69
Final conversion ($wt.\%$)	94	92	78	72
M_w(Daltons)	122825	119357	105760	96078
M_w/M_n	5.6	6.757	6.638	6.323

According to the reaction kinetics curves shown in Figures 38 to 40, the polymerization process can be roughly divided into three different intervals named intervals I

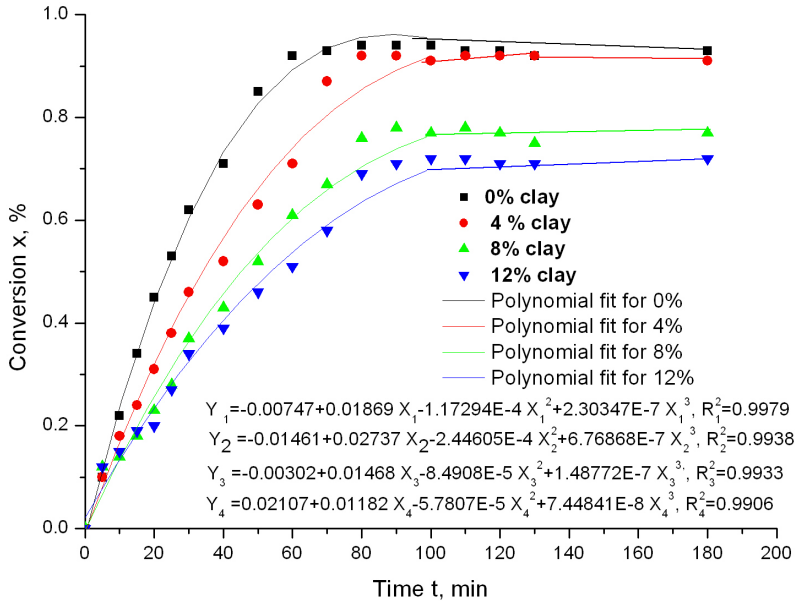


Figure 38: Conversion as a function of time at different SSC loadings. $10wt.\%$ hexadecane (based on monomer) was used in the miniemulsion process; $T = 70\,^{o}$C.

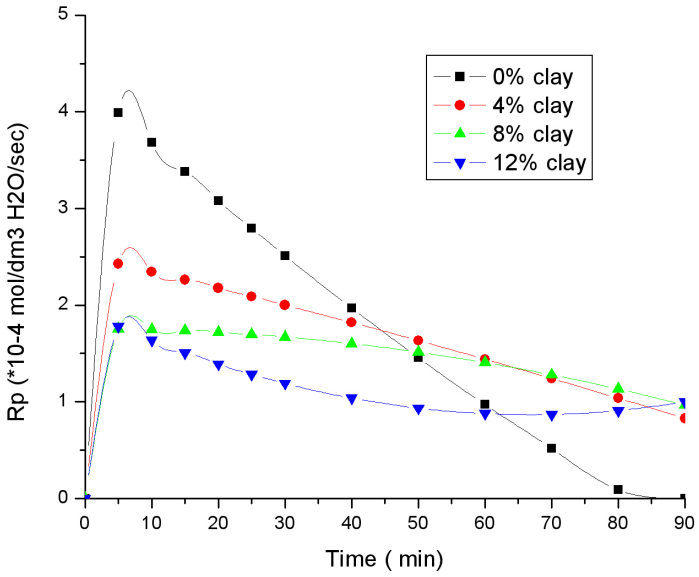


Figure 39: Rate of polymerization (Rp) as a function of polymerization time in the presence of SSC at different loadings. $10wt.\%$ hexadecane (based on the monomer) was used in the miniemulsion process; $T = 70\,^{o}$C

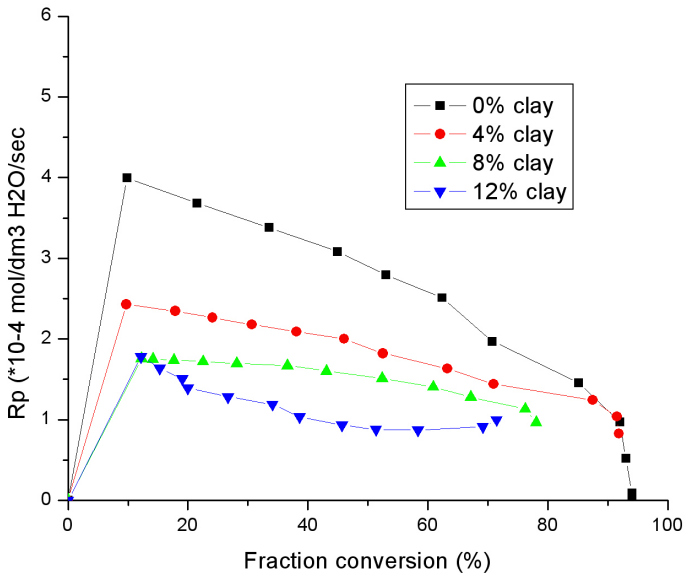


Figure 40: Rate of polymerization (Rp) as a function of fraction conversion in the presence of nanoclay (SSC) at different loadings. $10wt.\%$ hexadecane (based on monomer) was used in the miniemulsion process;$T = 70\,^{o}$C

(particle nucleation), III (particle growth) and IV (gel and glass effect), respectively. The interval I is the particles nucleation step, and in this interval an equilibrium radical concentration within every droplet is formed. The starting interval lasts for about 6min, which is slightly shorter than 8 minute [11] reported previously when a water-soluble initiator was used.

Compared to classical emulsion polymerization, miniemulsion polymerization generally shows different stages. For a classic emulsion polymerization, three different intervals, named intervals I (particle nucleation), interval II (monomer transferring), and interval III (particle growth) are usually observed [94]. A distinctive feature of miniemulsion polymerization, however, is that no interval II could be observed because the droplet nucleation is the dominating initiation mechanism, which results in a continual decrease of the monomer concentration so the polymerization rate after the initiation stage. The polymerization rates versus reaction times shown in Figures

39 and 40 clearly indicate that all polymerization systems, including pure styrene and the reaction systems containing high clay content, followed a typical miniemulsion polymerization process. It was also observed that the rate of polymerization for pure styrene miniemulsion systems decreased faster than that of miniemulsion system containing nanoclay particles. This suggests that nanoclay reduces the rate of monomer depleting inside the reaction site. As the reaction time was near to the time at the maximum conversion, the rate of polymerization (R_p) increased in the presence of nanoclay. In general, all these studies clearly suggest that the nanoclay introduced in the system has a hindered effect on the reaction rate and the fractional conversion.

7.3.2 Polymerization parameters before and after miniemulsion polymerization

As shown in Table 9, the number of miniemulsion droplets per unit of water, $N_{m,i}$ and $N_{p,f}$, decreased as the clay content was increased. This is in accordance with the decrease of the polymerization rate (R_p). Meanwhile, the average particle size and polydispersity index of the final latex particles rose with the increase of the nanoclay content. This suggests that a large inclusion of nanoclay within the latex particles causes disability of the emulsion droplets. On contrary, the average molecular weight Mw decreases when increasing the nanoclay content. The polydispersibility index of molecules, M_w/M_n, in the presence of nanoclay is greater than those in the absence of nanoclay, suggesting that the presence of nanoclay in the system increases the chain transfer or the termination of propagation radical chains. As a result, the addition of nanoclay hinders the rate of polymerization and the final conversion of styrene miniemulsion polymerization.

The effect of nanoclay on the number of the particle per unit water before and after polymerization provides important information about the miniemulsion stability and its nucleation mechanism. For a heterophase polymerization, homogeneous nucleation

(including micellar nucleation) and droplet nucleation are currently acceptable mechanisms by most researchers. The homogeneous nucleation occurs in surfactant-free emulsion polymerization, where the latex seeds are formed from aggregating oligomers in the water phase and the monomer is diffused to the nucleation site (water phase) [8]. Homogeneous nucleation is the second possible nucleation mechanism in miniemulsion polymerization as reported by Choi et al [25] (20% droplet nucleation), Chern et al [23] (50%-60% droplet nucleation) and Reimers and Schork[90] (95% droplet nucleation). Table 9 shows that the ratio of $N_{p,f}/N_{m,i}$ is greater than 1 in the case of pure styrene miniemulsion, suggesting some new particles were formed during the polymerization. Therefore, it can be concluded that both homogeneous nucleation and particle nucleation coexisted in the miniemulsion polymerization of pure styrene. The ratio of $N_{p,f}/N_{m,i}$ was close to 1 in the presence of 4% and 8% nanoclay, which indicates that the monomer droplet nucleation is the dominant mechanism at a low concentration of nanoclay. It is well know that the addition of nanoclay will cause a significant increase in the monomer viscosity, even can form a gel at high concentration of nanoclay. Because of the increase of the viscosity inside the monomer droplet in the presence of nanoclay, the molecular diffusion of both initiator and monomer from the reaction sites (oil droplet) to water phase could be significantly reduced. Consequently, the water phase nucleation is prohibited. Furthermore, it was found that $N_{p,f}/N_{m,i}$ was also greater than 1 when the organoclay content was increased to $12wt.\%$. It was also noted that both the particles size and polydispersity dramatically increased at such high clay concentration, suggesting that the polymerization system is unstable. As the small particles collide and aggregate to large aggregates during the polymerization, both $N_{p,f}$ and $N_{m,i}$ decrease so the ratio of $N_{p,f}/N_{m,i}$is different from a stable miniemulsion polymerization system. Table 9 also shows that the polydispersity of the final latex was slightly lower than the monomer droplets before the polymerization for all systems. The dependence of polymerization rate(R_p) on

the number of the droplet (unit droplet particle number) (N_p) is illustrated in Figure 41, and a relationship of R_p (at maximum) proportional to $N_p^{1.0}$ was established with a linear analysis. The exponent 1.0 agrees very well with the classical Smith-Ewart Kinetics [3].

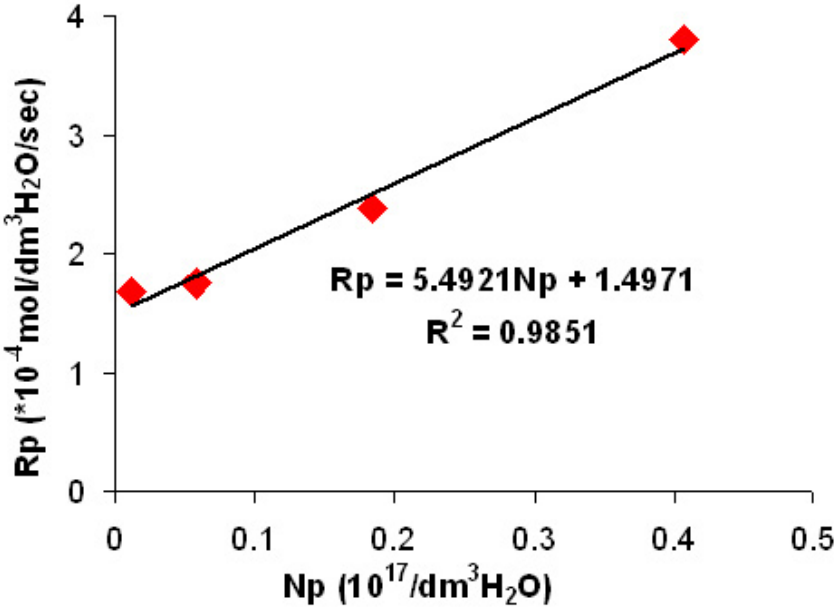


Figure 41: Polymerization rate (Rp) at maximum point as a function of number of particles per unit (Np) for styrene miniemulsion polymerization in the presence of SSC in different loadings

The effect of nanoclay addition on the active radical number per particle was studied and the results are shown in Figure 42. In the absence of nanoclay or at a low concentration of nanoclay content ($< 4\%$), is less than 0.5, which indicates that the particle initiation (Interval I) is still on the way at the maximum R_p. Combining these results with that illustrated in Figure 39 and 40, and the ratio of $N_{p,f}/N_{m,i}$ before and after polymerization, it can be concluded that the our polymerization system in the absence of nanoclay fits a typical styrene miniemulsion polymerization very well, in which the droplet nucleation is the dominating initiation mechanism, but the homogeneous nucleation also plays a minor role.

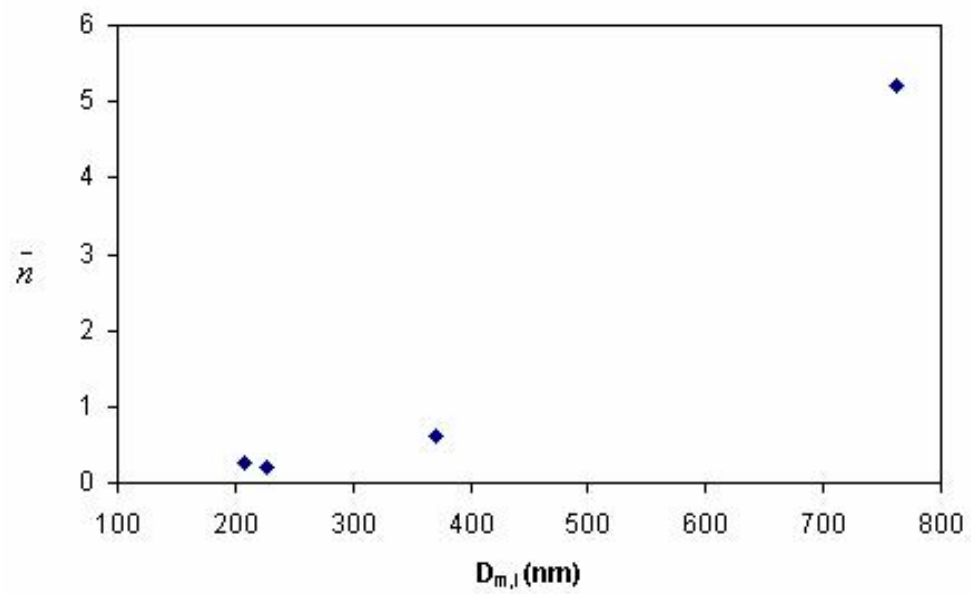


Figure 42: The number of average radicals in a droplet,$\bar{n}$, at maximum Rp as a function of the monomer particle diameter ($D_{m,i}$) for styrene miniemulsion at different loadings

Figure 39 also shows a typical miniemulsion polymerization curve for the clay content less than or equal to 4%. Different from a emulsion polymerization with three distinguished intervals, only interval I with an increasing R_p and interval III with a decreasing R_p appear, while interval II (a constant polymerization rate period) is absent. As we aforementioned, droplet nucleation mechanism was the dominant mechanism for the polymerization at this condition. This is further confirmed by the ratio of $N_{p,f}/N_{m,i}$ which is close to 1 at this instance (See table 9). However, when the nanoclay content was up to 8%, $\bar{n}$ (radical number per particle) was less than 1 but greater than 0.5 and $N_{p,f}/N_{m,i}$ slightly increased in comparison to that of 4% clay content, but it was still much smaller than the ratio obtained from pure styrene miniemulsion polymerization (See Table 9), which indicates that the particle nucleation plays a critical role in this case. On the one hand, the high viscosity of the monomer phase at 8% organoclay content could reduce the rate of both coupling

termination and disproportionation mechanism of living polymers in a droplet. On the other hand, the relatively large droplet formed by adding clay to the monomer could also increase the opportunity of two or more radicals co-exist in one monomer droplet. For these reasons, therefore, the $\bar{n}$ could be great than 1 for this case. It could therefore be concluded that the droplet nucleation play a predominating role, and the polymerization rate is determined by the reaction occurred inside the monomer droplets when clay is presented in the monomer droplets.

In contrary to the miniemulsion polymerization of styrene with 4% and 8% organoclay, the $\bar{n}$ enhanced dramatically when the nanoclay content increased to 12 $wt.\%$. In addition, it was also noted that, for the system containing 12 $wt.\%$, both the average particle size and the ratio of $N_{p,f}/N_{m,i}$ increased dramatically during the miniemulsion process. It was noted that small amount of polymer composite was deposited on the bottom of the reactor and stirrer surface, suggesting the system was not very stable at such high clay content. The increase of $\bar{n}$ may arise from two factors. First, the high viscosity at high clay content of monomer particles reduces the diffusion of free radicals if "cage effect" is not considered. Second, the particles with a large particle size are capable to have more free radicals inside than ones with a small particle size.

Table 9 also indicates that, for all the systems studied, the introduction of nanoclay not only reduced the rate of polymerization R_p but also resulted in a lower reaction conversion, lower M_w, and a greater latex particle size and particle size polydispersibility in comparison to that of pure styrene miniemulsion polymerization. It was also found that the particle nucleation mechanism is dominant if the nanoclay is presented inside the monomer droplets. However, in the absence of nanoclay, both droplet nucleation and homogeneous nucleation coexist although the homogeneous nucleation mechanism plays a minor role, which results in a increasing in the ratio of $N_{p,f}/N_{m,i}$. The main reason for a lower polymerization rate in the presence of

nanoclay is due to the destabilization of monomer droplet, which results in a decrease of the particle number in the aqueous phase (N_p). Furthermore, when particle nucleation is dominant, the increase in the monomer phase viscosity and the reduction in the diffusion rate of the living radicals and oligmer in the presence of nanoclay can further lower the propagation rate of the polymerization.

7.3.3 The effects of nanoclay chemistry and size on the miniemulsion polymerization of styrene

As discussed above, the miniemulsion polymerization rate and the properties of the final product can be dramatically affected by the addition of nanoclay particles. We have previously shown that the particle size of nanoclay influenced the morphology of the final latex, the efficiency of encapsulation of the nanoclay with polymer, and the stability of final latex particles [107, 108]. In order to further understand these factors, nanoclays with different particle sizes and chemistries were used and the effects of the nanoclay type on the miniemulsion stability were studied. The result is shown in Figure 43 and Table 10. Three OTAB-modified organoclays with different average particle sizes were selected. Figure 43 shows that the particle size and the polydispersity index (PDI) of the particles increased when increasing the clay content for all the systems. As shown in Table 10, the miniemulsions containing saponite are relatively stable. However, as shown in Figure 43, the particle size of emulsion droplets is affected by the type of nanoclay. For example, the droplet size with SSC (approximately 50 nm) is generally smaller than that with NSC (approximately 200 nm). The particle sizes of emulsion droplets containing MMT (approximately 450 nm) were mediate between that containing SSC and NSC , but the particle size polydispersibility is greater than other two miniemulsion systems. This can be attributed to the instability of miniemulsion in the presence of large MMT particles. This is different from small saponite particles, which can be easily encapsulated in the monomer droplets. The large MMT particles could only attach to the surface of

	SSC (50nm)		NSC (200nm)		MMT (450nm)	
Clay Content (%)	Oil dispersion viscosity	Emulsion stability	Oil dispersion viscosity	Emulsion stability	Oil dispersion viscosity	Emulsion stability
0.05	Low	Stable	Low	Stable	Middle (Gel)	Unstable
0.1	Low	Stable	Low	Stable	Middle (Gel)	Unstable
0.5	Low	Stable	Middle	Stable	High (Gel)	Unstable
1.0	Low	Stable	Middle	Stable	High (Gel)	Unstable

Table 10: The apparent viscosity of styrene dispersion and the emulsion stability at different clay contents(based on the weight of the monomer)

the monomer droplets, resulting in a more remarkable decrease in the miniemulsion stability. As shown in Table 3, the miniemulsion in the presence of MMT was unstable and high-viscosity gel-like monomer phase was observed before emulsification. The partial phase separation was also shown during the emulsification process. Due to the phase separation, the particle size measured by the light scattering is a mixture of pure monomer particles and MMT particles. This conclusion is supported by our previous studies [107, 108] that indicated that small nanoclay particles (approximately 100 nm) can be encapsulated in the polymer latex, but large nanoclay particles can only be suspended in the final latex system by adhering to the latex particle surface. We also previously found that no stable emulsion could be synthesized using montmorillonite because of their large plate size of 450 nm.

7.4 Conclusion

The effects of nanoclay on the polymerization kinetics of styrene miniemulsion have been investigated. The nanoclay introduced in this study not only decreased the rate of polymerization Rp but also resulted in lowering the reaction conversion, lowering M_w, increasing the polydispersibility as well as the latex particle size in comparison to that in a pure styrene miniemulsion polymerization. For the system containing

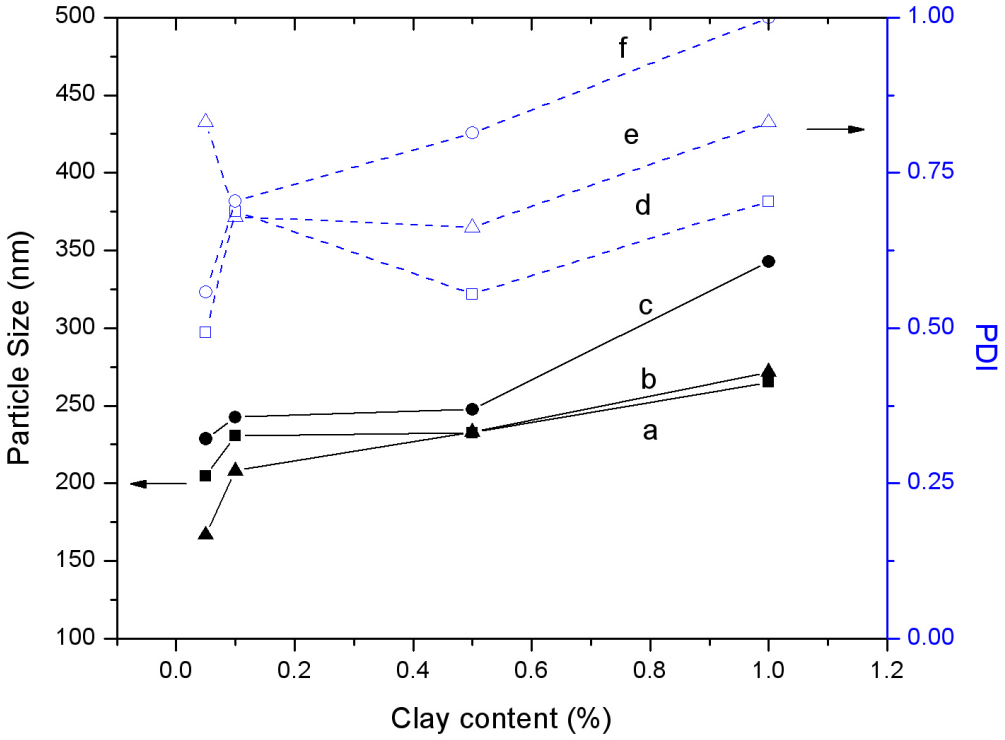


Figure 43: The miniemulsion droplet size (solid lines) and polydispersity index (PDI) (dashed lines). The droplet size of miniemulsion a: in the presence of SSC (50nm); b: in the presence of MMT (450nm); c: in the presence of NSC (200nm); The polydispersity of miniemulsion d: in the presence of SSC (50nm); e: in the presence of MMT (450nm); f: in the presence of NSC (200nm)

less than 12 $wt.\%$ saponite, the polymerization followed a typical miniemulsion polymerization mechanism, and the particle nucleation was dominating. The rate of polymerization decreased in interval III for all systems with the saponite clay due to the depleting of monomer inside the reaction site. The introduction of nanoclay favored the droplet nucleation by increasing the viscosity of the monomer phase and retarding the monomer diffusion from the monomer droplet. On the contrary, in the absence of nanoclay, the homogeneous nucleation mechanism acted as a second nucleation mechanism. However, in the presence of a high concentration of nanoclay (12 $wt.\%$), the miniemulsion was unstable and the increased droplet size during miniemulsion polymerization process led to a larger ratio of $N_{p,f}/N_{m,i}$. Generally, in the presence of nanoclay, due to the increase in the particle size and the decrease in the particle number in the aqueous phase (N_p), the polymerization rate (R_p) decreased. Furthermore, the enhancement of the monomer phase viscosity in the inclusion of organoclay lowered the reactivity of the radicals and the living polymer. However, it was also found that large clay particles, such as montmorillonite, could remarkably reduce the miniemulsion stability.

CHAPTER VIII

THE THERMAL AND PHYSICAL PROPERTIES OF POLYSTYRENE AND POLYSTYRENE-BUTYLACRYLATE COPOLYMER NANOSAPONITE COMPOSITE FILMS

Previous research focuses on the synthesis approach, morphology controlling, miniemulsion stability, and its polymerization mechanism for the synthesis of polystyrene nanoclay composites in an aqueous phase. Generally, a stable water-based suspension of polymer encapsulated nanoclay composite has been successfully achieved via a one-step miniemulsion polymerization. The nanoclay is exfoliated in polymer nanocomposites, based on the analysis of the XRD patterns. The following question is whether the introduction of the well-dispersed and exfoliated nanoclay leads to better properties of polymer nanocomposite. Therefore, in this chapter we examine the impact of nanoclay on the mechanical and thermal properties of the PS and PSBA composite films in comparison to pure PS and PSBA films. The results show that the nanoclay reinforces PS and PSBA composite films in almost all the aspects of mechanical properties. With regard to thermal properties, the inclusion of nanoclay does not affect the T_g of composites, but improves the thermal stability characterized by the enhancement of T_m.

8.1 Introduction

Depending on the intercalation degree of organoclay, the polymer clay composite (using organoclay as precursors) is divided into four types. The conventional composite, where the clay acts as conventional filler, has a tactoid structure. Therefore, their rigidity can be improved but they usually sacrifice strength, elongation and toughness. Different from the conventional polymer clay composite, nanocomposite is that clay nanolayers disperse in the polymer matrix in an intercalated, an ordered exfoliated or a disordered exfoliated form. In an intercalated nanocomposite, the clay intercalated space is fixed and can be detected by X-ray. The average gallery height of the exfoliated nanocomposite is determined by a clay loading. The difference between the ordered and disordered nanocomposite is that the former exhibits a crystal structure but the later shows an amorphous structure. Generally, the greater the intercalated degree of nanoclay composite, the better the improvement of nanocomposite [59]. The polymer nanoclay composite, by the incorporation of the intercalated and exfoliated nanoclay, produces a remarkable property improvement in comparison to the pure engineering plastics and conventional microcomposites. Improvements include superior strength, elongation, toughness and possible thermal stability. The encapsulation of nanoclay into the polymer particles provides better interaction of nanoclay and polymer. A well-dispersed and exfoliated nanoclay in polymer nanoclay composites which we synthesized should have better properties in comparison to that of pure polymer plastics and microcomposites.

In this chapter, two types of polymer systems: polystyrene and polystyrene-co-butylacrylate nanocomposites were synthesized via miniemulsion polymerization and the impact of clay SSC on the physical and thermal properties of PS and PSBA nanocomposite films were evaluated. As we know, styrene-based polymers are widely used in almost every plastic application. It is available in both opaque and transparent films, sheets, foams, elastomers and is used as components of alloys/blends and

thermoplastic elastomers [93]. For example, ABS (acrylonitrile-butadiene-tyrene) is a common thermoplastic used to make light, rigid, molded products such as piping, musical instruments, golf club heads, automotive body parts, wheel covers, enclosures, protective head gear, and toys including LEGO bricks because of its resistance and toughness. Because the synthesis of ABS requires a high-pressure reactor, it is not investigated in this research. Another important styrene-based polymer, such as acrylic resins or acrylate polyesters, have broad applications in water-based coating and painting by blending with Polyurethane dispersions. Acrylic latex are lower in cost and have excellent exterior durability [115]. But it has a low abrasive resistance and toughness. Therefore, PSBA nanoclay composite films which we synthesized are expected to have better toughness and abrasive resistance.

8.2 Experiment

8.2.1 Materials

Plasticizer dioctyl phthalate(1,2-Benzenedicarboxylic acid,dioctyl ester) was purchased from Aldrich Chemical Inc. Styrene and BA monomer were purified by washing with 5 wt.% NaOH solution followed by de-ionized water until pH of 7, and then was distilled under reduced pressure and stored in the refrigerator prior to use. For all other materials refer to previous chapters.

8.2.2 Procedures

Composite latex via miniemulsion polymerization: SSC was surface modified by VBTAC following the same procedure in previous chapters. Then, polystyrene latexes, in the presence of 0 wt.%, 2 wt.%, and 4 wt.% of SSC (based on the weight of the styrene monomer) were prepared by following a typical run mentioned in previous chapters. The recipe to synthesize a water-based suspension of PSBA copolymer nanocomposite in the presence of the different content of SSC is shown in Table 11. Oil phase A, composed of 1.0 g of co-stabilizer hexadecane and 0.2 g of AIBN, 6 g of

monomer styrene and 4 g of monomer BA, and a varied amount of SSC (0-4 wt.%) based on the weight of the monomer styrene), was subjected to a magnetic stirring at room temperature for 30 minutes. The mixture was then exposed to ultrasonification for 4 min. Following that, oil phase A was poured into an aqueous phase B comprising of 1 g of TX-405 in 100 ml of water. Thereafter the mixture was under a vigorous mechanical stirring in an ice bath for 30 minutes. Fianlly, the miniemulsion composed of A and B was prepared by homogenization under ultrasonification for another 3 minutes and ready for subsequent polymerization. The miniemulsion polymerization was carried out by the same procedure as in previous chapters.

Table 11: The Basic Recipe for the Miniemulsion Polymerization of PSBA/Clay Nanocomposite Latex Particles

Mixture	Ingredient	Amount (g)	Percentage in total(wt.%)	percentage to monomer(wt.%)
Oil Phase	styrene Butyl acrylate styrene/BA (60:40 wt.%)	12	10.4	100
	Organo-saponite (SSC)	$0 - 0.48$	$0 - 0.4$	$0 - 4.0$
	Hexadecane	1.2	1.0	10.4
	AIBN	0.24	0.2	2.0
Water Phase	Tx-405	1.0	0.9	8.3
	Water	100	87.0	833.3

The preparation of composite films and the measurement of their physical and thermal properties: Polystyrene nanosaponite latex was firstly vacuum-dried at 80 ^{o}C until a constant weight. Then,1 g of the composite and 0.1 g of plasticizer dioctyl phthalate (based on the weight of the dried composite) was dissolved in 20 ml THF. Thereafter, the solution was stirred and then sat for several hours until a clear solution was formed. Finally, the resultant mixture was cast into a glass dish and kept overnight in the fume hood at room temperature and under slow air circulation. PSBA nanosaponite latex was directly cast into a glass dish and followed the same drying process as that of PS composite films. After a clean film

was formed, the film was pealed off from the glass dish and ready for physical testing.

The film was cut into dimensions of $70 \times 15mm$ ($length \times width$). Then samples were conditioned at $50.0 \pm 2.0\%$ relative humidity and $23.0 \pm 1.0\,^{o}$C for 1 day. The conditioned samples were tested on an Instron 4400R Universal Testing maching (Model 1122, Instron Corp., USA). The cross speed used for polystyrene composite film was 250 mm/min and that for PSBA composite film was 750 mm/min. Because of the break length limitation of the machine, the cross speed applied for PS and PSBA composite films' measurement must be kept different. The applied load (f) was recorded as a function of sample elongation $(l - l_0)$. The tensile strength $\sigma = f/a$, and $\epsilon = (l - l_0)/l_0$, respectively, where a is the sample cross-sectional area, l_0 is the sample initial length and l is the length at breaking. The Young modulus was obtained from the linear slope of stress versus strain curve during the initial $5 - 10\%$ strain. The averages of tensile energy adsorpltion (TEA), tensile strength and strain were obtained using four specimens for each measurement. Differential scanning calorimetry (DSC) of PS and PSBA composite films was carried out on a Pyris 1 Perkin-Elmer Differential Scanning Calorimeter, with a heating rate of $10\,^{o}$C/min under nitrogen.

8.3 Result and discussion

8.3.1 Physical properties of composite films

To ascertain the impact of nanoclay on the physical properties of the polymer nanoclay composite films, the tensile strength, TEA, strain and modulus were measured and their results are shown in Figures 44, 45, 46, 47. As shown in Figure 44, both PS and PSBA copolymer composite films in the presence of 4 wt.% clay approximately exhibit a two-fold increase in tensile strength in the absence of clay, while the tensile strength of the composites in the presence of 2 wt.% clay is slightly improved, which

indicates that the tensile strength of composite strongly depends on the nanoclay content. In Figure 45, the strains for both PS and PSBA composite films are enhanced slightly by increasing the amount of nanoclay, which indicates that the clay content impacts more on strength than elongation. Tensile energy adsorption (TEA) is the work done when a specimen is stressed to rupture in tension and is measured by the integral of the tensile strength over the range of tensile strain from zero to maximum strain. Figure 46 illustrates that the TEA of composites has an approximate linear relationship with the clay content. Figure 47 demonstrates that the Young modulus of PS film increases when increasing the clay content and its tendency is similiar as the tensile strength curve. However, the Young modulus of PSBA film is firstly decreased and then slightly increased when increasing the amount of nanoclay. The Young modulus is measured at the initial stage (5-10% strain). It assumes that stress and stain at the initial stage has a linear relationship according to Hooke's law. However, this linear relationship for a pure PS composite is not applied for the complex PSBA system. When comparing PS with PSBA copolymer nanoclay composite, although PSBA composite film was operated at three-folder crosss peed of PS film during the measurements, PSBA still exhibits much longer strain, higher TEA and slightly lower tensile strength than PS composite film. This indicates that the introduction of soft polymer butylacrylate improves the mechanical properties in comparison with pure PS composite film.

In summary, PS composite films exhibit an increasing tensile strength, toughness and elongation properties when increasing the clay content. PSBA composite films also show an increasing tensile strength and elongation property, which indicates that nanoclay reinforces the polymer film in almost all aspects of mechanical properties. As previous mentioned, conventional polymer clay composites containing aggregated nanoclayer tactoids improve rigidity (modulus), but they often sacrifice strength and elongation. However, in respect to polymer nanoclay composites, our

results demonstrate that the introduction of organoclay would lead to both the improvement of strength and tougheness, which agrees well with Chang et al's results [21]. The exfoliated clay layers distribute uniformly inside the polymer matrix and they provide tremendous surface areas of the clay, which faciliates stress transfer to the reinforcement phase allowing for such tensile and toughing improvement as reviewed by Lebaron et al [59].

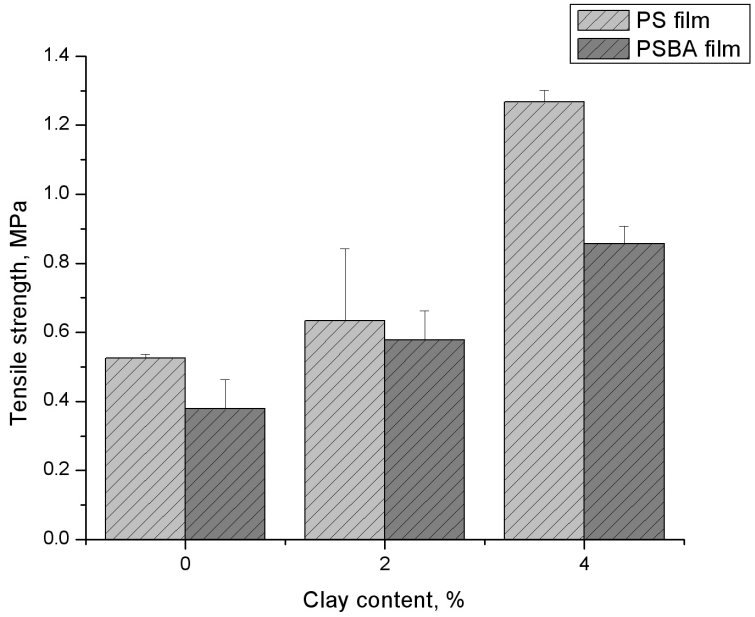


Figure 44: Tensile strength of PS and PSBA nanoclay composite films in the presence of different contents of nanoclay

8.3.2 Thermal properties of composite films

Figure 48 shows the effect of clay content on the crystallization behavior of polystyrene. Two exothermic peaks are illustrated both in the absence of nanoclay and the presence of nanoclay. One peak is around 19 ^{o}C for all three clay loadings, which indicates that the introduction of organoclay does not impact the crystallization temperature (T_g) of PSBA composite film. But the melting temperatures (T_m) (49.2 ^{o}C) of nanocomposites in the presence of 4 wt.% is slightly greater than that (47.2 ^{o}C and 46.8 ^{o}C)

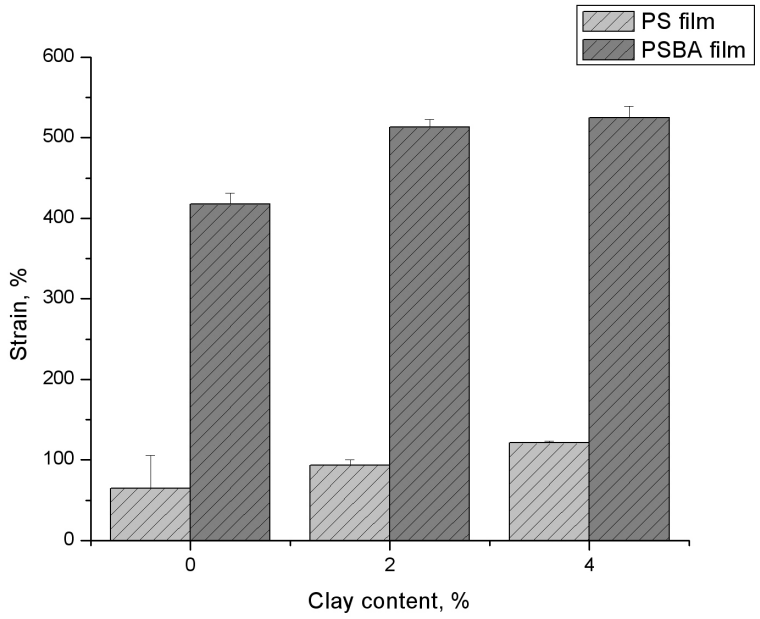


Figure 45: Strain of PS and PSBA nanoclay composite films in the presence of different contents of nanoclay

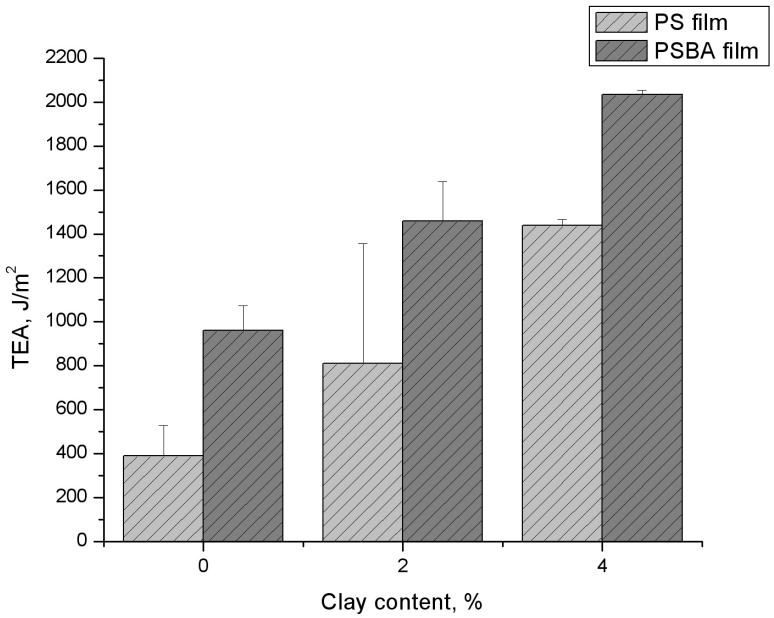


Figure 46: TEA of PS and PSBA nanoclay composite films in the presence of different contents of nanoclay

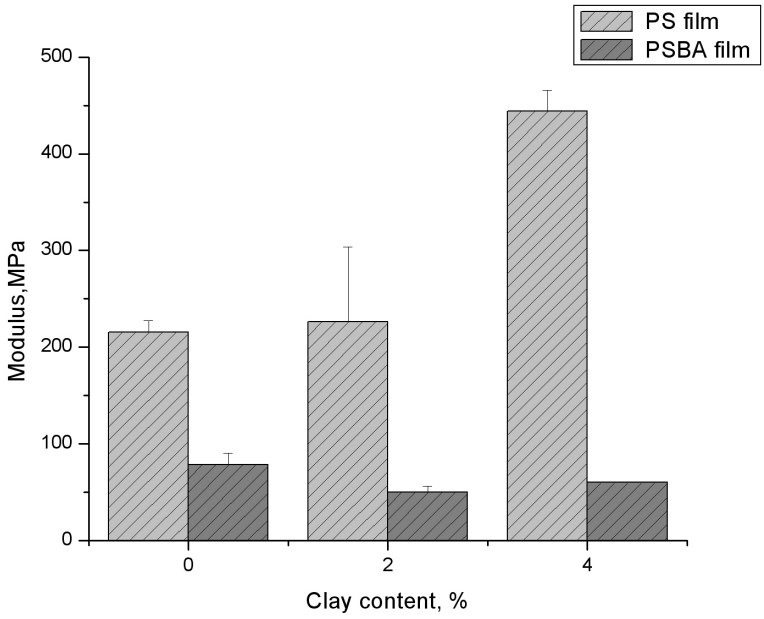


Figure 47: Modulus of PS and PSBA nanoclay composite films in the presence of different contents of nanoclay

in the absence of organoclay and in the presence of 2 wt.% clay, respectively. It can be concluded that a low loading of organoclay does not affect the melting temperature (T_m) and a high content of organoclay slightly increases T_m of the composite film. This result agrees well with other research's result, in which they prove that organo-MMT does not affect the value of T_g of PSBA composite [74].

The impact of the introduction of organoclay on the thermal properties of PS composite films was also investigated as shown in Figure 49. No T_g peak appears in the curves of all the systems, which indicates that an amorphous polystyrene matrix was formed. It may attribute to a large amount of the plasticizer (10 wt.% based on the weight of composite), which prevents the polystyrene crystallizing due to the strong interaction between the plasticizer dioctyl phthalate and polystyrene. This phenomena is also reported by Ma et al.[69]. They reported that the interactions between the plasticizer and the polymer starch prevented starch molecules from crystallizing. It was also found that the melting temperature is enhanced with increasing

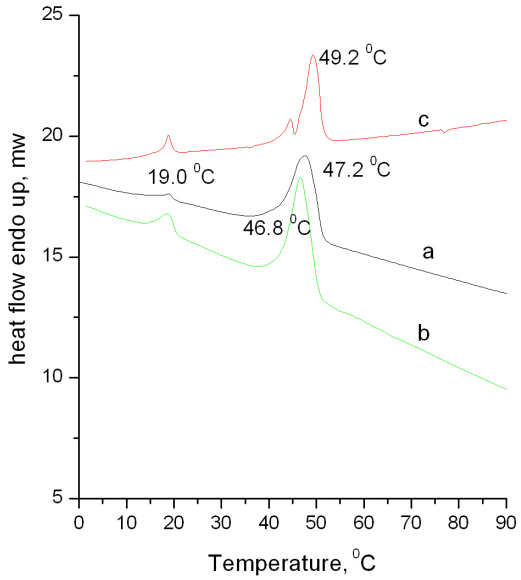


Figure 48: DSC of PSBA nanoclay composite films in the presence of different contents of nanoclay: a 0%clay; b 2%clay; c 4%clay

clay content, as shown in Figure 49, T_m is 238.8 ^{o}C and 199.8 ^{o}C in the presence of 4 wt.% and 2 wt.% organoclay, respectively. T_m is 192.7 ^{o}C in the absence of organoclay, which indicates that the thermal stability was improved by the inclusion of organoclay. Moreover, we attempted to make the PS and PSBA composite films in the presence of large amount of organoclay ($> 4wt.\%$). However, PS and PSBA composite films at a large clay content were brittle and they could not be easily peeled off from glass dishes.

8.4 Conclusions

This chapter aims to study the impact of the amount of clay SSC on the physical and thermal properties of PS and PSBA copolymer nanocomposite films. In the aspect of mechanical properties of polymer nanoclay composite films, nanoclay improved all the mechanical properties of PS and PSBA copolymer. PS composite films exhibit an increasing tensile strength, toughness and elongation properties when increasing the

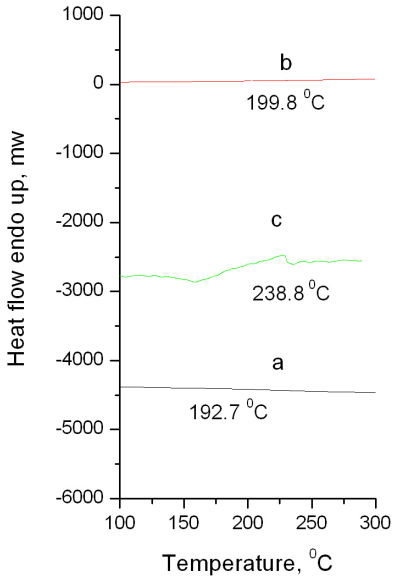


Figure 49: DSC of PS nanoclay composite films in the presence of different contents of nanoclay: a 0%clay; b 2%clay; c 4%clay.

clay content, and PSBA composite films exhibit an increasing tensile strength and elongation properties. However, the Young modulus of PSBA nanocomposite films in the presence of nanoclay is lower than that of pure PSBA nanocomposite films. Comparing the PS and PSBA composite films under the same clay content, the PSBA copolymer nanoclay composite films illustrate a dramatic elongation improvement, a relatively higher TEA and a relatively lower tensile strength than that of PS composite films. In the aspect of thermal properties of polymer nanoclay composite films, the introduction of nanoclay does not influence T_g of PSBA copolymer nanocomposite. T_g of PS composite films disappear if a large amount (10 wt% based on the weight of dired composite) of plasticizer prevents polymer re-crystallization. However, the nanoclay improves thermal stability by the enhancement of T_m of PSBA and PS composite films.

CHAPTER IX

OVERALL CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

The synthesis of stable latex of polymer encapsulated nanoclay composite has been very challenging. First of all, we attempted to seek a feasible approach to synthesize a stable water-based suspension of polymer nanoclay composite by using MMT-KSF as the clay, which has a large particle size (approximately 450nm) and a broad particle size distribution (the range of the particle size from several nanometers to several micrometers). However, through a variety of emulsion and miniemulsion polymerization methods in combination with different surface modification approaches of nanoclay, we failed to produce a stable aqueous suspension due to the large particle size of clay MMT-KSF. The particle size of nanoclay is critical to produce a stable aqueous suspension of polymer nanoclay composite. To make a stable aqueous suspension of polymer nanoclay composite, two types of saponite from the smectite family were considered as the clay candidates based on their suitable particle sizes. They are NSC with the average particle size of 200nm and SSC with the average particle size of 50nm and a more uniform particle size distribution. Furthermore, the synthesized method, miniemulsion polymerization presents advantages in producing a stable latex because of its ability to produce the nanoparticles dispersed into a continuous medium; and encapsulating inorganic particles into the polymer droplets due to its predominating droplet nucleation mechanism. In general, the particle size of the clay,

the well-selected surface modification method of the clay and the optimization of polymerization parameters all play important roles on stability, encapsulation efficiency and morphology formation.

Initially, a stable water-based polymer nanoclay colloid containing anisotropic NSC platelets was successfully synthesized by miniemulsion polymerization. The polymer-nanoclay composites have an intercalated structure and the final latex suspensions are stable up to 5 wt.% clay in the polymer. The treatment of NSC by cation OTAB is critical not only for intercalation but also for hydrophobically modification of the clay surface, so clay particles can be easily dispersed in the monomer phase during the miniemulsion polymerization process. The costabilizer has a synergistic effect on stability of final latex. However, although a stable aqueous suspension of polymer nanoclay composite was achieved, the organophilic clay was not encapsulated inside the polymer particles, and they firmly adhered onto the polystyrene latex particle surface due to the large particle size of NSC.

As discussed in Chapter VI, When saponite with the average particle size of 50 nm was pre-modified by a monomer reactive cationic surfactant VBTAC, a stable aqueous polystyrene nanoclay composite latex containing large amounts (up to 30%) of organo-saponite was obtained. The correct pretreatment chemistry and the particle size of nanoclay are two critical factors for encapsulation and exfoliation of nanoclay inside the latex particles. The morphologies of final latex particles and their melting films in the presence of the unmodified and the modified nanoclay were investigated. The results further proved that VBTAC- modified nanoclay was exfoliated and encapsulated inside the polymer latex particles. The polystyrene/nanosaponite composite particles principally consisted of spherical particles with a core-shell structure and with an average particle size less than 100 nm. However, a number of hemispherical or truncated particles existed in the system as well. In the absence of nanoclay, these assymetric particles are hollow particles. This mechanism which forms hollow

particles with a hemispherical or bowl structure contributes to the phase separation in the presence of large amounts of hydrophobe hexadecane. In the presence of nanoclay, in the hemispherical or truncated (crescent) particle, a thin layer of the platelet saponite clay adhered to the truncated plane. Both phase separation and inclusion of nanoclay contribute to the formation of hemispherical or truncated (crescent) particles. Meanwhile, the intercalated nanoclay with a proper particle size could function as a template to form polymer/clay composite particle with a unsymmetrical morphology.

In previous research discussed in Chapter V, we found that nanoclay affects the kinetics of styrene miniemulsion by reducing the polymerization rate and the fractional conversion. Therefore, in chapter VII, the mechanism of styrene miniemulsion polymerization in the inclusion of SSC was extensively investigated. The result shows that the nanoclay introduced in the system not only decreased the rate of polymerization R_p but also resulted in lowering reaction conversion, lowering M_w, increasing polydispersibility and the latex particle size in comparison to that of pure styrene miniemulsion polymerization. The decrease in the polymerization rate and fractional conversion when adding organoclay is mainly caused by the destabilization of the miniemulsion in the presence of organoclay. The increase in the monomer phase viscosity and the decrease in the diffusion rate of the monomer and the living polymer inside the monomer droplet are also the feasible reason for the reduction of polymerization rate.

Finally, as illustrated in chapter VIII, the impact of SSC concentration on the physical and the thermal properties of PS and PSBA copolymer nanocomposite films was investigated. The results show that nanoclay reinforces PS and PSBA copolymer nanoclay composite film in almost all aspects of mechanical properties. By Comparing the mechanical properties of the PS and PSBA composite films under the same clay concentration, PSBA copolymer nanoclay composite films illustrate a dramatic

elongation improvement, a relative higher TEA and a relative lower tensile strength than that of PS composite. Nanoclay also improves thermal stability by the enhancement of T_m of PSBA and PS composite films, but it doesn't have any effect on the T_g.

9.2 Future work

There are several forms of experiments offered as recommendations for future endeavor. Firstly, due to the time limitation, we only investigated the physical properties of composite films by using the synthesized polymer composite latex. As we reviewed in Chapter II, the barrier properties should be greatly improved and the composites in aqueous form have many advantages over those in bulk and solvent form. The stable water-based latex of polymer nanoclay composites is expected to have great potential in the area of water-based barrier paper coating. First, the recommended future research can be:

- to apply this stable water-based polymer composite latex as a coating formula of paper barrier coating.
- to investigate the impact of the nanoclay on a variety of paper or paperboard properties such as water vapor transmission rate of paper and paper board, contact angle and cobb value, grease resistance test, surface strength of paper, strength properties.
- to compare the properties by using this aqueous composite latex of the organoclay encapsulated inside the polymer, of the organoclay directly mixed with polymer latex, and of the unmodified clay directly mixed with polymer latex

Second, a self-assembling approach to synthesize core-shell structural particles is the new morphology of latex found in this research. How to synthesize the composite

particles with a core-shell structure in a uniform particle size distribution and minimize the fraction of pure polymer particles have not been studied. The research in this dissertation provides a viable approach to produce asymmetric particles with a hemispherical or truncated spherical morphology. It is valuable to investigate how to produce a large amount of and pure hemispherical particles or selectively separate the particles with different morphologies. The approach to modify the clay surface in different chemistry and seeking a template with uniform particle size distribution can be recommended to produce the polymer latex particles with an asymmetric morphology.

Finally, although the impact of nanoclay on the miniemulsion polymerization was investigated in Chapter VII, future research can be extended to examine the impact of nanoclay on the behavior of the active radicals in miniemulsion polymerization by using the oil soluble initiator, the effect on the miniemulsion stability and the nucleation mechanism.

REFERENCES

[1] Aizpurua, I., Amalvy, J., Cal, J. D., and Barandiaran, M., "High solid content miniemulsion polymerization of vinyl acetate in a continuous stirred tank reactor," *Polymer*, vol. 42, no. 4, pp. 1417–1427, 2001.

[2] Akiva, U. and Margel, S., "Surface-modified hemispherical polystyrene/polybutyl methacrylate composite particles," *Journal of Colloid and Interface Science*, vol. 288, no. 1, pp. 61–70, 2005.

[3] Anderson, C. D., Sudol, E., and M.S., E.-A., "Elucidation of the miniemulsion stabilization mechanism and polymerization kinetics," *Journal of applied polymer science*, vol. 90, no. 14, pp. 3987–3993, 2003.

[4] Antonietti, M. and Landfester, K., "Polyreactions in miniemulsions," *Progress in polymer science*, vol. 27, no. 4, pp. 689–757, 2002.

[5] Arshady, R., "Suspension, emulsion, and dispersion polymerization: A methodological survey," *Colloid and polymer science*, vol. 270, no. 8, pp. 717–732, 1992.

[6] Asua, J. M., *Polymeric dispersions:principles and applications*. Dordrecht, the Netherlands: Kluwer Academic, first ed., 1997.

[7] Asua, J., Rodriguez, V., sudol, E., and El-asser, M., "The free radical distribution in emulsion polymerization using oil-soluble initiators," *Journal of polymer science: part A: polymer chemistry*, vol. 27, no. 11, pp. 3569–3587, 1989.

[8] Asua, J. M., "Miniemulsion polymerization," *Progress in polymer science*, vol. 27, no. 7, pp. 1283–1346, 2002.

[9] Bailey, S., "The status of clay mineral structures," *Clay and clay minerals proc. 14th National conferences*, pp. 1–23, 1966.

[10] Bakhshaee, M., Pethrick, R., Rashid, H., and Sherrington, D., "Encapsulation of carbon blacks into suspension polymerized copolymers," *Polymer communications(Guldford England)*, vol. 26, pp. 185–192, June 1985.

[11] Bechthold, N. and Landfester, K., "Kinetics of miniemulsion polymerization as revealed by calorimetry," *Macromolecules*, vol. 33, no. 13, pp. 4682–4689, 2000.

[12] Bechthold, N., Tiarks, F., Willert, M., Landfester, K., and Antinietti, M., "Miniemulsion polymerization:applications and new materials," *Macromolecular symposium*, vol. 151, no. 1, pp. 549–522, 2000.

[13] Bourgeat-Lami, E., Insulaire, M., Rechlusa, S., Perro, A., Rayaine, S., and Duguet, E., "Nucleation of polystyrene latex particles in the presence of γ-methacryloxypropyltrimethoxysilane: Functionalized silica particles," *Journal of Nanoscience and nanotechnology*, vol. 6, no. 2, pp. 432–444, 2006.

[14] Bourgeat-Lami, E. and Lang, J., "Encapsulation of inorganic particles by dispersion polymerization in polar media. 1. silica nanoparticles encapsulated by polystyrene," *Journal of Colloid and Interface Science*, vol. 197, no. 2, pp. 293–308, 1998.

[15] Bourgeat-Lami, E. and Lang, J., "Encapsulation of inorganic particles by dispersion polymerization in polar media. 2. effect of silica size and concentration on the morphology of silica-polystyrene composite particles," *Journal of Colloid and Interface Science*, vol. 210, no. 2, pp. 281–289, 1999.

[16] Buback, M. and Kuchta, F., "Ariation of the propagation rate coefficient with pressure and temperature in the free-radical bulk polymerization of styrene," *Macromolecular Chemistry and Physics*, vol. 196, no. 6, pp. 1887–1898, 1995.

[17] Burns, A., Ow, H., and Wiesner, U., "Fluorescent core-shell silica nanoparticles: towards lab on a particle architectures for nanobiotechnology," *Chemical society review*, vol. 35, no. 11, pp. 1028–1042, 2006.

[18] Capek, I., "On the role of oil-soluble initiators in the radical polymerization of micellar systems," *Advances in Colloid and Interface Science*, vol. 91, no. 2, pp. 295–334, 2001.

[19] Capek, I., *Nanocomposite structures and dispersions: science and technology-fundamental principles and colloidal particles*. Studies in interface science, UK: Elsevier, first ed., 2006.

[20] Carrado, K. A., "Synthetic organo- and polymer-clays: preparation, characterization, and materials applications," *Applied Clay Science*, vol. 17, no. 1-2, pp. 1–23, 2000.

[21] Chang, J., An, Y. U., and Sur, G. S., "Poly(lactic acid) nanocomposites with various organoclays. i. thermomechanical properties, morphology,and gas permeability," *Journal of polymer science: Part B: Polymer Physics*, vol. 41, pp. 94–103, 2002.

[22] Chavez, J. L., Wong, J. L., Jovanovic, A. V., Sinner, E. K., and Duran, R. S., "Encapsulation in sub-micron species: a short review and alternate strategy for dye encapsulation," *Nanobiotechnology, IEE Proceedings*, vol. 152, pp. 73–84, Apr. 2005.

[23] Chern, C. S., Liou, Y. C., and Chen, T. J., "Particle nucleation loci in styrene miniemulsion polymerization using alkyl methacrylates as the reactive cosurfactant," *Macromolecular chemistry and physics*, vol. 199, no. 7, pp. 1315–1322, 1998.

[24] Chern, C. and Liou, Y., "Styrene miniemulsion polymerization initiated by 2,2'-azobisisobutyronitrile," *Journal of polymer science: part A:polymer chemistry*, vol. 37, no. 14, pp. 2537–2550, 1999.

[25] Choi, Y., El-Aasser, M. S., Sudol, E., and Vanderhoff, J., "Polymerizatio of styrene miniemulsion," *Journal of polymer science:chemistry edition*, vol. 23, no. 12, pp. 2973–2987, 1985.

[26] Cooper, R., "Barrier coatings for paper and paperboard," *Paper technology*, vol. 31, no. 1, pp. 34–36, 1990.

[27] Delgado, J., El-Aasser, M., and Vanderhoff, J., "Miniemulsion copolymerization of vinyl acetate and butyl acrylate. i. differences between the miniemulsion copolymerization and the emulsion copolymerization processes.," *Journal of polymer science Part A: polymer chemistry*, vol. 24, no. 7, pp. 861–874, 1986.

[28] Ding, X., Zhao, J., Liu, Y., Zhang, H., and Wang, Z., "Silica nanoparticles encapsulated by polystyrene via surface grafting and in situ emulsion polymerization," *Materials Letters*, vol. 58, no. 25, pp. 3126–3130, 2004.

[29] Du, Y., Tomohiro, T., Zhang, G., Nakamura, K., and Kodaka, M., "Biotinylated and enzyme-immobilized carrier prepared by hetero-bifunctional latex beads," *chemical communications*, no. 6, pp. 616–617, 2004.

[30] Du, Y.-Z., Ma, G.-H., Ni, H.-M., Nagai, M., and Omi, S., "Morphological studies in thermally initiated emulsion (co)polymerization without conventional initiators," *Journal of Applied Polymer Science*, vol. 84, no. 9, pp. 1737–1748, 2002.

[31] Du, Y.-Z., Tomohiro, T., and Kodaka, M., "Synthesis of hemispherical poly(2-hydroxylethyl methacrylate-co-methyl methacrylate)/poly(styrene-co-glycidyl methacrylate) composite particles with heterobifunctional groups by soap-free seeded emulsion polymerization," *Macromolecules*, vol. 37, no. 3, pp. 803–812, 2004.

[32] Erdem, B., Sudol, D. E., Dimonie, V. L., and El-Aasser, M. S., "Encapsulation of inorganic particles via miniemulsion polymerization. i. dispersion of titanium dioxide particles in organic media using oloa 370 as stabilizer," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 38, no. 24, pp. 4419–4430, 2000.

[33] Erdem, B., Sudol, D. E., Dimonie, V. L., and El-aasser, M. S., "Encapsulation of inorganic particles via miniemulsion polymerization. ii. preparation and characterization of styrene miniemulsion droplets containing tio$_2$ particles," *Journal of polymer science: partA:polymer chemistry*, vol. 38, pp. 4431–4440, 2000.

[34] Erdem, B., Sudol, D. E., Dimonie, V. L., and El-Aasser, M. S., "Encapsulation of inorganic particles via miniemulsion polymerization. ii. preparation and characterization of styrene miniemulsion droplets containing tio_2 particles," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 38, no. 24, pp. 4431–4440, 2000.

[35] Erdem, B., Sudol, D. E., Dimonie, V. L., and El-Aasser, M. S., "Encapsulation of inorganic particles via miniemulsion polymerization. iii. characterization of encapsulation," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 38, no. 24, pp. 4441–4450, 2000.

[36] Espiard, P. and Guyot, A., "Poly(ethyl acrylate) latexes encapsulating nanoparticles of silica: 2. grafting process onto silica," *Polymer*, vol. 36, no. 23, pp. 4391–4395, 1995.

[37] Essawy, H., Badran, A., Youssef, A., El-Fetoh, A., and El-Hakim, A., "Synthesis of poly(methylethacrylate)/montmorillonite nanocomposites via in situ intercalative suspension and emulsion polymerization," *polymer bulletin*, vol. 53, pp. 9–17, Nov. 2004.

[38] Fontenot, K. and Schork, F., "Batch polymerization of methyl methacrylate in mini/macroemulsions," *Journal of applied polymer science*, vol. 49, no. 4, pp. 633–655, 1993.

[39] Gilbert, R. G., *Emulsion polymerization: a mechanistic approach*. Collod science, London, San diego, New york, Boston, Sydney, Tokyo: Harcourt Brace & company, first ed., 1995.

[40] Gong, F., Feng, M., Zhao, C., Zhang, S., and Yang, M., "Particle configuration and mechanical properties of poly(vinyl chloride)/montmorillonite nanocomposites via in situ suspension polymerization," *polymer testing*, vol. 23, pp. 847–853, 2004.

[41] Gooch, J. W., *Lead-based paint handbook*. Topics in applied chemistry, New York: Plenum Press, .

[42] Gooch, J., Dong, H., and Schork, F., "Waterborne oil-modified polyurethane coatings via hybrid miniemulsion polymerization," *Journal of applied polymer science*, vol. 76, no. 1, pp. 105–114, 2000.

[43] Han, S.-H., Ma, G.-H., Du, Y.-Z., Omi, S., and Gu, L.-X., "Preparation of hemispherical poly(4-vinylpyridine-co-butyl acrylate)/poly(styrene-co-butyl

acrylate) composite microspheres by seeded preswelling emulsion polymerization," *Journal of Applied Polymer Science*, vol. 90, no. 14, pp. 3811–3821, 2003.

[44] HARKINS, W. D., "General theory of mechanism of emulsion polymerization. ii," *Journal of polymer science*, vol. 5, no. 2, pp. 217–251, 1950.

[45] HARRIPI, P. and O'REALS, D., "Measurement of liporoteins using the zetasizer 3000." Application notes, June 1998.

[46] HERRERA, N. N., LETOFFE, J.-M., PUTAUX, J.-L., DAVID, L., and BOURGEAT-LAMI, E., "Aqueous dispersions of silane-functionalized laponite clay platelets. a first step toward the elaboration of water-based polymer/clay nanocomposites," *Langmuir*, vol. 20, pp. 1564–1571, 2004.

[47] HUAI, N. Y. and ROUTH, A. F., "Formation of liquid core-polymer shell microcapsules," *Soft matter*, vol. 2, no. 11, pp. 940–949, 2006.

[48] HUANG, X. and BRITTAIN, W. J., "Synthesis and characterization of pmma nanocomposites by suspension and emulsion polymerization," *Macromolecules*, vol. 34, pp. 3255–3260, Feb. 2001.

[49] ISODA, K., KURODA, K., and OGAWA, M., "Interlamellar grafting of γ-methacryloxypropylsilyl groups on magadiite and copolymerization with methyl methacrylate," *chemistry of materials*, vol. 12, no. 6, pp. 1702–1707, 2000.

[50] JANG, L., CHUL, M., and LEE, D., "A new hybrid nanocomposite prepared by emulsion copolymerization of abs in the presence of clay," *Journal of polymer science part B: polymer physics*, vol. 39, no. 6, pp. 719–727, 2001.

[51] J.YEUM, Q. S. and DENG, Y., "Poly (vinyl acetate)/silver nanocomposite microspheres prepared by suspension polymerization at low temperature," *Macromolecular materials and engineering*, vol. 290, no. 1, pp. 78–84, 2005.

[52] KIM, J. W., CHOI, H. J., and JUON, M., "Synthesis and electrorheological characterization of emulsion polymerization san-clay nanocomposite suspension," *Macromolecular symposium*, vol. 155, no. 1, pp. 229–237, 2000.

[53] KIM, J. W., KIM, S. G., CHOI, H., and JUON, M., "Synthesis and electrorheological properties of polyaminiline-na$^+$-montmorillonite suspensions," *Macromolecular rapid communication*, vol. 20, no. 8, pp. 450–452, 1999.

[54] KORNMANN, X., *Synthesis and characterization of thermoset-clay nanocomposites*. PhD dissertation, Material- och produktionsteknik / Polymerteknik, Aug. 1999.

[55] KUMAR, G. and BEAUDOIN, S., "Undercut removal of micrometer-scale particles from surfaces," *Journal of the Electrochemical Society*, vol. 153, no. 2, pp. 175–181, 2006.

[56] Landfester, K., Bechthold, N., Tiarks, F., and Antonietti, M., "Formation and stability mechanisms of polymerization miniemulsions," *Macromoleculars*, vol. 32, no. 16, pp. 5222–5228, 1999.

[57] Landfester, K. and Ramirez, L. P., "Encapsulated magnetite particles for biomedical application," *Journal of Physics: Condensed Matter*, vol. 15, no. 15, pp. 1345–1361, 2003.

[58] Landfester, K., Bechthold, N., Forster, S., and Antonietti, M., "Evidence for the preservation of the particle identity in miniemulsion polymerization," *Macromolecular Rapid Communications*, vol. 20, no. 2, pp. 81–84, 1999.

[59] Lebaron, P. C., Wang, Z., and Pinnavaia, T. J., "Polymer-layered silicate nanocomposites: An overview," *Applied Clay Science*, vol. 15, no. 1, pp. 11–29, 1999.

[60] Lelu, S., Novat, C., graillat, C., Guyot, A., and Bourgeat-Lami, E., "Encapsulation of an organic phthalocyanine blue pigment into polystyrene latex particles using a miniemulsion polymerization process," *Polymer International*, vol. 52, no. 4, pp. 542–547, 2003.

[61] Liu, G., Zhang, L., Gao, C., and Qu, X., "Copolymerization of styrene with n-phenyl maleimide in the presence of montmorillonite," *Journal of Applied Polymer Science*, vol. 98, no. 5, pp. 1932–1937, 2005.

[62] Liu, J., Kuo, J.-C., and Fang, M., "Synthesis of chiral polymers containing the acetoxybornyl group and their applications on the asymmetric induction," *Journal of Applied Polymer Science*, vol. 45, no. 9, pp. 1587–1594, 2003.

[63] liu, X., Kim, J., Wu, J., and Eisenberg, A., "Bowl-shaped aggregates from the self-assembly of an amphiphilic random copolymer of poly(styrene-co-methacrylic acid)," *Macromolecules*, vol. 38, no. 16, pp. 6749 – 6751, 2005.

[64] Lovell, P. A. and El-Aasser, M. S., *Emulsion polymerizaton and emulsion polymers*. West Sussex PO 19 IUD, England: John Wiley & Sons, Inc., Baffins lane, Chichester, first ed., 1997.

[65] Loxley, A. and Vincent, B., "Preparation of poly(methylmethacrylate) microcapsules with liquid cores," *Journal of colloid and interface science*, vol. 208, no. 1, pp. 49–62, 1998.

[66] Lu, Y., Yin, Y., and Xia, Y., "Three-dimensional photonic crystals with non-spherical colloids as building blocks," *Advanced Materials*, vol. 13, no. 6, pp. 415–420, 2001.

[67] Luo, Y., Liu, B., Wang, Z., Gao, J., and Li, B., "Butyl acrylate raft polymerization in miniemulsion," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 45, no. 11, pp. 2304–2315, 2007.

[68] Luo, Y., Rong, M., Zhang, M., and Friedrich, K., "Surface grafting onto sic nanoparticles with glycidyl methacrylate in emulsion," *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 42, no. 15, pp. 3842–3852, 2004.

[69] Ma, X., Yu, J., He, K., and Wang, N., "The effects of different plasticizers on the properties of thermoplastic starch as solid polymer electrolytes," *Macromolecular Materials and Engineering*, vol. 292, no. 4, pp. 503–510, 2007.

[70] Martens, C. R., *Emulsion and water-soluble paints and coatings*. Unitied States of America: Reinhold publishing corporation, first ed., 1964.

[71] McDonald, C. J., Bouck, K. J., and Chaput, A. B., "Emulsion polymerization of voided particles by encapsulation of a nonsolvent," *Macromolecules*, vol. 33, no. 5, pp. 1593–1605, 2000.

[72] Moon, S. D., Kang, S., and Bu, J., "Fabrication of polymeric microlens of hemispherical shape using micromolding," *Optical Engineering*, vol. 41, no. 9, pp. 2267–2270, 2002.

[73] Moraes, R. P., Santos, A., Olivelra, P., Fatima, C., Do-Amoral, M., Volera, T., and Demarquette, N., "Poly(styrene-co-butyl acrylate)-brazilian montmorillonite nanocomposites, synthesis of hybrid latexes via miniemulsion polymerization," *Macromolecular Symposia*, vol. 245-246, no. 1, pp. 106–115, 2006.

[74] Moraes, R. P., Santos, A. M., Souza, F. C. T., d. Amaral, M., Valera, T. S., and Demarquette, N. R., "Poly(styrene-co-butyl acrylate)-brazilian montmorillonite nancomposites,synthesis of hybrid latexes via minimeulsion polymerization," *Macromolecular Symposium*, vol. 245-246, pp. 106–115, 2006.

[75] Moustafa, A. B., Hakim, A., and Mohamed, G., "Some parameters affecting the emulsifier-free emulsion polymerization of vinyl acetate," *journal of applied polymer science*, vol. 63, no. 2, pp. 239–246, 1997.

[76] Nie, Z., Xu, S., Seo, M., Lewis, P., and Kumacheva, E., "Polymer particles with various shapes and morphologies produced in continuous microfluidic reactors," *Journal of the American Chemical Society*, vol. 127, no. 22, pp. 8055–8063, 2005.

[77] Noh, M., Jang, L., and Lee, D., "Intercalation of styrene-acrylonitrile copolymer in layered silicate by emulsion polymerization," *Journal of applied polymer science*, vol. 74, no. 1, pp. 179–188, 1999.

[78] Noh, M. and Lee, D., "Comparison of characteristics of san-mmt nanocomposites prepared by emulsion and solution polymerization," *Journal of applied polymer science*, vol. 74, no. 12, pp. 2811–2819, 1999.

[79] Nomura, M. and Suzuki, K., "The kinetic and mechanistic role of oil-soluble initiators in micro- and macroemulsion polymerizations," *Industrial & Engineering Chemistry Research*, vol. 44, no. 8, pp. 2561–2567, 2005.

[80] ODIAN, G., *Principles of polymerization*. John Wiley & Sons, Inc., Hoboken, New Jersey, fourth ed., June 2004.

[81] Okada, A., Kawasumi, M., Usuki, A., Kojima, Y., Kurauchi, T., and Kamigaito, O., "Nylon 6-clay hybrid," *Material resource society proceedings*, vol. 171, pp. 45–50, 1990.

[82] Okaniwa, M., "Synthesis of poly(dimethylsiloxane) and poly(butadiene) composite particles and the properties of their grafted polymer particles," *Polymer*, vol. 41, no. 2, pp. 453–460, 2000.

[83] Padget, J. C., "Polymer for water-based coatings-a systematic overview," *Journal of coatings technology*, vol. 66, no. 839, pp. 89–105, 1994.

[84] Paul, S., ed., *Surface coating science and technology*. Chichester,New York,Weinheim, Brisbane,Toronto, singapore: John wiley &sons, second ed., 1996.

[85] Paunov, V. N. and Cayre, O. J., "Supraparticles and"janus" particles fabricated by replication of particle monolayers at liquid surfaces using a gel trapping technique," *Advanced Materials*, vol. 16, no. 9-10, pp. 788–791, 2004.

[86] Perro, A., Reculusa, S., Ravaine, S., Bourgeat-Lami, E., and Duguet, E., "Design and synthesis of janus micro- and nanoparticles," *Journal of materials chemistry*, vol. 15, no. 1, pp. 51–60, 2005.

[87] Pinnavaia, T. and G.W.Beall, eds., *Polymer-clay nanocomposites*. Wiley series in polymer science, Chichester, England ; New York : Wiley, 2001.

[88] Qiu, G., Wang, Q., Wang, C., Lau, W., and Guo, Y., "Polystyrene/fe_3o_4 magnetic emulsion and nanocomposite prepared by ultrasonically initiated miniemulsion polymerization," *Ultrasonics Sonochemistry*, vol. 14, no. 1, pp. 55–61, 2007.

[89] Ramirez, L. P. and Landfester, K., "Magnetic polystyrene nanoparticles with a high magnetite content obtained by miniemulsion processes," *Macromolecular Chemistry and Physics*, vol. 204, no. 1, pp. 22–31, 2003.

[90] Reimers, J. and Schork, F. J., "Robust nucleation in polymer-stabilized miniemulsion polymerization," *Journal of polymer science*, vol. 59, no. 12, pp. 1833–1841, 1996.

[91] Saifullin, R. S., *Physical chemistry inorganic polymeric and composite materials*. New York: Ellis Horwood, 1992.

[92] Savolainen, A., ed., *Surface coating science and technology*. Papermaking science and technology: book 12, Atlanta, Georgia: [Helsinki] : published in cooperation with the Finnish Paper Engineers Association, first ed., 1998.

[93] Schlechter, M., "Styrenics." http://www.bccresearch.com, Oct. 2001.

[94] Schork, F. J., Luo, Y., Smulders, W., Russum, J. P., Butt, A., and K.Fontenot, *Miniemulsion polymerization*, vol. 175, ch. Polymer particles, pp. 129–256. Heidelberg: Springer-Verlag, 2005.

[95] Shulkin, A. and Stōver, H. D., "Photostimulated phase separation encapsulation," *Macromolecules*, vol. 36, no. 26, pp. 9836–9839, 2003.

[96] Sun, Q. and Deng, Y., "Synthesis and characterization of polystyrene-encapsulated laponite composites via miniemulsion polymerization," *Macromolecular Materials and Engineering*, vol. 289, no. 3, pp. 288–295, 2004.

[97] Sun, Q., Schork, J. F., and Deng, Y., "Water-based polymer/clay nanocomposite suspension for improving water and moisture barrier in coating," *Composites Science and Technology*, vol. 67, no. 9, pp. 1823–1829, 2007.

[98] Sungberg, D. C. and Durant, Y. G., "Latex particle morphology, fundamental aspects: A review," *Polymer Reaction Engineering*, vol. 11, no. 3, pp. 379–432, 2003.

[99] Tang, P. L., Sudol, E., Silebi, C., and El-Aasser, M., "Miniemulsion polymerization-a comparative study of preparative variables," *journal of applied polymer science*, vol. 43, no. 6, pp. 1059–1208, 1991.

[100] Tang, P., Sudol, E., Adams, M., El-Asser, M., and Asua, J., "Seeded emulsion polymerization of n-butyl acrylate utilizing miniemulsions," *Journal of applied polymer science*, vol. 42, no. 7, pp. 2019–2026, 1991.

[101] Teresa, B., "Hydrophilic core-shell microspheres: A suitable support for controlled attachment of proteins and biomedical diagnostics," *Macromolecular Bioscience*, vol. 5, no. 12, pp. 1145–1168, 2005.

[102] Theng, B., *Formation and properties of clay-polymer complexes*. Amsterdam ; New York: Elsevier Scientific Pub. Co., 1979.

[103] Thomas, P., ed., *Waterborne & solvent based surface coating resins and their applications*. Surface coatings technology, Chichester,New York,Weinheim, Brisbane,Toronto, singapore,london: John wiley & sons in association with Sita technology limited, first ed., 1998.

[104] Tiarks, F., Landfester, K., and Antonietti, M., "Preparation of polymeric nanocapsules by miniemulsion polymerization," *Langmuir*, vol. 17, no. 3, pp. 908–918, 2001.

[105] Tiarks, F., Landfester, K., and Antonietti, M., "Encapsulation of carbon black by miniemulsion polymerization," *Macromolecular chemistry and physics*, vol. 202, no. 1, pp. 51–60, 2001.

[106] Tong, X., Zhao, H., Tang, T., Feng, Z., and Huang, B., "Preparation and characterization of poly(ethyl acrylate)/bentonite nanocomposite by in situ emulsion polymerization," *Journal of polymer science:part A:polymer chemisitry*, vol. 40, pp. 1706–1711, Mar. 2002.

[107] Tong, Z. and Deng, Y., "Synthesis of water-based polystyrene-nanoclay composite suspension via miniemulsion polymerization," *Industrial and Engineering Chemistry Research*, vol. 45, no. 8, pp. 2641–2645, 2006.

[108] Tong, Z. and Deng, Y., "Synthesis of polystyrene encapsulated nanosaponite composite latex via miniemulsion polymerization," *Polymer*, vol. 48, no. 15, pp. 4337–4343, 2007.

[109] Tsavalas, J. G., *A molecular level investigation of hybrid miniemulsion polymerization*. PhD dissertation, Georgia Institute of Technology, School of chemcial and biomolecular engineering, Oct. 2001.

[110] Tullmin, M., "Coatings-historical items." www.corrosion-club.com/historycoatings.htm, October 2007.

[111] Ugelstad, J., El-Aasser, M. S., and Vanderhoff, J. W., "Emulsion polymerization: Initiation of polymerization in monomer droplets," *Journal of Polymer Science Polymer Letters Edition*, vol. 11, no. 8, pp. 503–513, 1973.

[112] Vaia, R. A., Ishii, H., and Giannelis, E. P., "Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates," *Chemistry of materials*, vol. 5, no. 12, pp. 1694–1696, 1993.

[113] Vera, P., "Trends in coatings developments for industrial surfaces," *Plant engineering*, vol. 36, no. 14, pp. 50–56, 1982.

[114] Vera-nissi, P. and Lahti, J., "New water-based barrier coatings for paper and paperboard," *Appita Journal*, vol. 54, no. 2, pp. 106–115, 2001.

[115] Wicks, Z. W., Jones, F. N., Pappas, S. P., and Wicks, D. A., *Organic coatings science and technology*. Wiley Interscience, The United States of America: A John Wiley& Sons, INC., third ed., 2007.

[116] Wu, Z., Zhou, C., and Qi, R., "The preparation of phenolic resin/montmorillonite nanocomposites by suspension condensation polymerization and their morphology," *polymer composite*, vol. 23, pp. 634–646, Aug. 2002.

[117] Xu, M., Choi, Y., Kim, Y., Wang, K., and Chung, I., "Synthesis and characterization of exfoliated poly(styrene-co-methyl methacrylate)/clay nanocomposites via emulsion polymerization with amps," *Polymer*, vol. 44, no. 20, pp. 6387–6395, 2003.

[118] Yariv, S. and Cross, H., eds., *Organo-clay complexes and interactions*. New York: Marcel Dekker, first ed., c2002.

[119] Yeum, J. and Deng, Y., "Synthesis of high molecular weight poly(methyl methacrylate) microspheres by suspension polymerization in the presence of silver nanoparticles," *colloid and polymer science*, vol. 283, pp. 1172–1179, Aug. 2005.

[120] Yoshinaga, K., Nakashima, F., and Nishi, T., "Polymer modification of colloidal particles by spontaneous polymerization of surface active monomers," *Colloid & Polymer Science*, vol. 277, no. 2-3, pp. 136–144, 1999.

[121] Yu, D., An, J., Bae, J., Ahn, S., Kang, S., and Suh, S., "Preparation of titanium dioxide/poly(methyl methacrylate-co-n-butyl acrylate-co-methacrylic acid) hybrid composite particles via emulsion polymerization," *Journal of Applied Polymer Science*, vol. 97, no. 1, pp. 72–79, 2005.

[122] Zhang, K., Chen, H., Chen, X., Chen, Z., Cui, Z., and Yang, B., "Monodisperse silica-polymer core-shell microspheres via surface grafting and emulsion polymerization," *Macromolecular materials and engineering*, vol. 204, no. 4, pp. 380–385, 2003.

[123] Zhang, S., Zhou, S., Weng, Y., and Wu, L., "Synthesis of sio_2/polystyrene nanocomposite particles via miniemulsion polymerization," *langmuir*, vol. 21, no. 6, pp. 2124–2128, 2005.

[124] Zhong, C. J. and Maye, M. M., "Core-shell assembled nanoparticles as catalysts," *Advanced Materials*, vol. 13, no. 19, pp. 1507–1511, 2001.